Markers of Crude Oil Migration through Low-Maturity Organic-Rich Pathways

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Declaration

I hereby certify that this work, and the contents thereof, is my own, except where otherwise acknowledged, and that it is original and has not been submitted previously for a degree at this, or any other university.

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Abstract

Maturity and source assessment anomalies have been observed particularly in Tertiary/deltaic oils which have migrated through immature, organic-rich sediments. The occurrence of unsaturated hydrocarbons (olefins) and carboxylic acids in crude oils has been previously reported, though there is limited published quantitative data. A two-part study identifies these uncommonly reported compounds in sets of field and laboratory simulated 'migrated' crude oils, in order to investigate their potential as migration-contamination markers, useful for helping to resolve many oil assessment anomalies.

In the field study, 29 apparently non-biodegraded crude oils from three well-known Tertiary deltas (Beaufort-Mackenzie, Kutei Basin, and Niger Delta) were investigated. In the laboratory study, a simulation of oil migrating through an immature organic-rich rock was carried out by pumping a mature North Sea crude oil through steel HPLC columns packed with organic-rich Kimmeridge Clay mudstone of varying particle sizes: 4 mm-1 mm, 1 mm-63 µm, and <63 µm. Samples of the resulting 'migrated' oils were analyzed for the presence, concentrations and distributions of these typically low-abundance compounds.

Olefins (*n*-alkenes, diasterenes and triterpenes) were detected in nearly all field samples, with summed concentrations ranging from <5 ppm to ~300 ppm. They were considered to have been dissolved from immature, organic-rich sedimentary sequence during migration as suggested by dissimilarities in the *n*-alkene to *n*-alkane distributions, and the presence of other olefins (e.g. diasterenes and hopenes) characteristic of immature organic matter. Linear acids (up to 6500 ppm) and C_{30}-C_{33} hopanoic acids (from <1 ppm to ~120 ppm) were detected, with the hopanoic acids exhibiting variable isomer distributions.

An increase in the abundance of olefins and also a relative enrichment in short-chain- (C_{12}-C_{19}) acids in the laboratory 'migrated' oils was observed. The acid profiles from the oils that had passed through the finest (<63µm) mudstone size fractions were different from those of the others, indicating that surface area and/or permeability differences were likely causative factors.

The results suggest that relatively high abundances of olefins and carboxylic acids in many of the studied non-biodegraded Tertiary deltaic oils are an indication of the occurrence of migration-contamination and that the extent, and actual signatures of this may be affected by variations in rock properties (e.g. permeability) and presence of faults and/or fractures within the migration route, as well as the organic richness of these carrier sequences.

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Dedication

I dedicate this thesis to Mr Nnamdi Oriuwa- a most supportive and committed husband who always finds me when I seem to be drifting away; and to Dr Lawrence Arinze – my father who has inspired me to this height through his love and quest for his children's education.

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Preface

The structure of this thesis has been designed to devise new methods and improved approaches to the characterisation and correlation of Tertiary deltaic hydrocarbons. Both the newly proposed and previous ideas are introduced and reviewed in Chapters One and Two respectively.

Geochemical assessment methods used for a suite of representative oils from Tertiary Deltas worldwide, as well as procedures used for the simulated migration experiments and methods of analysis of the collected 'migrated' oils, are presented in the following Chapter Three.

In Chapter Four, the results of the general molecular marker analyses, particularly the olefin and carboxylic acid distributions in the representative oils are shown, interpreted and discussed. Quantitative comparisons of the relative abundance and distribution of selected migration markers (olefins and acids), as well as those of the conventional hydrocarbon (saturates and aromatics) markers in produced, case study oils are also examined and presented in this chapter.

Likewise, a brief introduction to the laboratory migration simulation experiments, description of the study samples and results obtained using the combined 'simulation-rare marker' approach, are presented in Chapter Five. Here, possible 'contamination' of the artificially-migrated North Sea oil portions by soluble organic components of the organic-rich Kimmeridge Blackstone, is indicated and discussed in a typical Tertiary deltaic context.

Finally, Chapter Six presents the overall conclusions drawn from the findings of the project, alongside suggestions for future research work in order to further improve knowledge and understanding of the processes and factors that control the effects of secondary migration on oil molecular marker compositions in many petroleum provinces of the world, particularly in the Tertiary deltas.

Chapter 1 Introduction

1.0.Research Overview

Biomarkers are one of the most important components of crude oils and sediments that are used for petroleum exploration purposes. Their abundance and distribution have been extensively applied by geologists and geochemists to the characterisation of petroleum, source rocks, depositional environments of source organic matter as well as other well-known characteristics (Hoffman *et al.*, 1984, Tissot and Welte, 1984, Brooks, 1986a, Peters and Moldowan, 1993). However, their application to detecting migration pathways and migration effects on crude oil composition are relatively limited (Philp and Gilbert, 1986, Jaffé *et al.*, 1988a, Thompson and Kennicutt II, 1990, Ukpabio *et al.*, 1994, Curiale and Bromley, 1996a, Curiale and Frolov, 1998, Curiale, 2002, Hwang *et al.*, 2002).

The assessment of a crude oil in order to ascertain important features of its source rock assumes that the constituents of the oil are derived from the source rock – the organic-rich sedimentary rock units from which the oil was first expelled (Curiale, 1993). However, this theory does not hold where the components of the oil are different from those present in the source rock. This can be partly due to a process whereby the migrating oil acts as a solvent for non-source-derived components during transport from its source to the reservoir (Thompson and Kennicutt II, 1990, Curiale and Frolov, 1998). This phenomenon termed, in this study, as migration-contamination has been widely reported to occur in many oil-producing provinces of the world, along with their characteristic compositional alteration effects. Although significant discoveries have been made concerning the use of geochemical markers in oil as possible indicators of this process (e.g. Curiale and Bromley, 1996a, Curiale, 2002, Hwang *et al.*, 2002, Curiale *et al.*, 2005, Curiale, 2006, Li *et al.*, 2008), more studies are continually being undertaken to elucidate the processes that lead to this occurrence during migration.

This study focuses on the effects of secondary migration on the composition of crude petroleum via a mechanism which often modifies the usual biomarker profile of certain produced oils of the world, thereby resulting in spurious oil assessment data. The following sections of this chapter establish the context and significance of the study.

1.1. Background

Over the past several decades, biomarker profiling of petroleum has been a common tool for oil-oil and oil-source rock correlations as well as for the appraisal of source rock attributes such as thermal evolution, lithology, source organic matter, depositional environment, kerogen type and maturity (Peters and Moldowan, 1993, Curiale, 1995, Hughes and Dzou, 1995, Bartolomé *et al.*, 2007, Li *et al.*, 2008). It has also been used for investigation of the extent of oil biodegradation, oil maturity, source and migration (Brooks, 1986a, Jaffé *et al.*, 1988a, Curiale, 2002, Watson *et al.*, 2002). The application of biomarkers by virtue of their presence and relative abundance in oil has been based mainly on the assumption that the hydrocarbon profile of any oil is imprinted by its source. However, sometimes, the source-related biomarker signatures of some petroleum is observed to be transformed thereby making the assessment of oil and source correlation difficult or impracticable (Curiale, 1991, Curiale and Bromley, 1996a, Curiale, 2002, Hwang *et al.*, 2002, Bartolomé *et al.*, 2007). These assessment anomalies, observed in several oils from around the world, have fuelled renewed interest in the study of 'unusual' biomarker or organic components in geologic samples along with their increasingly routine applications to various aspects of petroleum assessments in recent times. These compounds may have, in the past, been simply ignored or overlooked either as a result of their unpopularity in geochemical studies, presumed scarcity and/or low concentration in oils due to lack of adequate separation techniques, or lack of knowledge of their presence in these samples.

1.1.1. *The Problem*

The composition of petroleum is affected by four major factors: source organic matter, thermal maturation, migration and in-reservoir alteration. Among these processes, the migration factor is still poorly understood, and finding ways to establish this has been the focus of active research by many workers (e.g. Bonilla and Engel, 1986, Curiale and Bromley, 1996b). Although a general knowledge of oil migration processes has been available for some years (e.g. Tissot and Welte, 1984), many uncertainties, such as the complexity and the effect of the process on the biomarker distributions of the migrated oil, still remain (Jaffé *et al.*, 1988b).

Three major processes of petroleum migration, with their individual composition alteration mechanisms, have been studied and reported; they include geochromatography, (e.g. Silverman, 1965, Leythaeuser *et al.*, 1984, Brothers *et al.*, 1991); migrational fractionation

(e.g. Thompson, 1987, Thompson, 1988, Larter and Mills, 1991, Dzou and Hughes, 1993, van Graas *et al.*, 2000), and migration-contamination (e.g. Jaffé *et al.*, 1988b, Morelos-Garcia *et al.*, 1993, Curiale and Bromley, 1996b, Curiale and Frolov, 1998, Curiale, 2002). It is well-known that petroleum migration along or through a geologic stratum could lead to possible compositional changes in the produced oil, condensate or gas as shown in Figure 1.1. This is expected since mobile crude oil is a 'solvent' and interacts, to some extent, with the active organic/mineral surfaces of the permeable rocks. Given a suitably active petroleum system in place, adequate contact time between the oil and the organic mineral surfaces, and good quality carrier structure, the solubilisation of indigenous organic matter by the migrating oil is expected. This occurrence can, hypothetically, impart a different or altered molecular signatures to the migrating or reservoired fluids, as illustrated in a similar scenario in Figure 1.1 (e.g. Trindade and Brassell, 1992, Curiale, 1995, Curiale and Bromley, 1996a, Curiale, 2002).

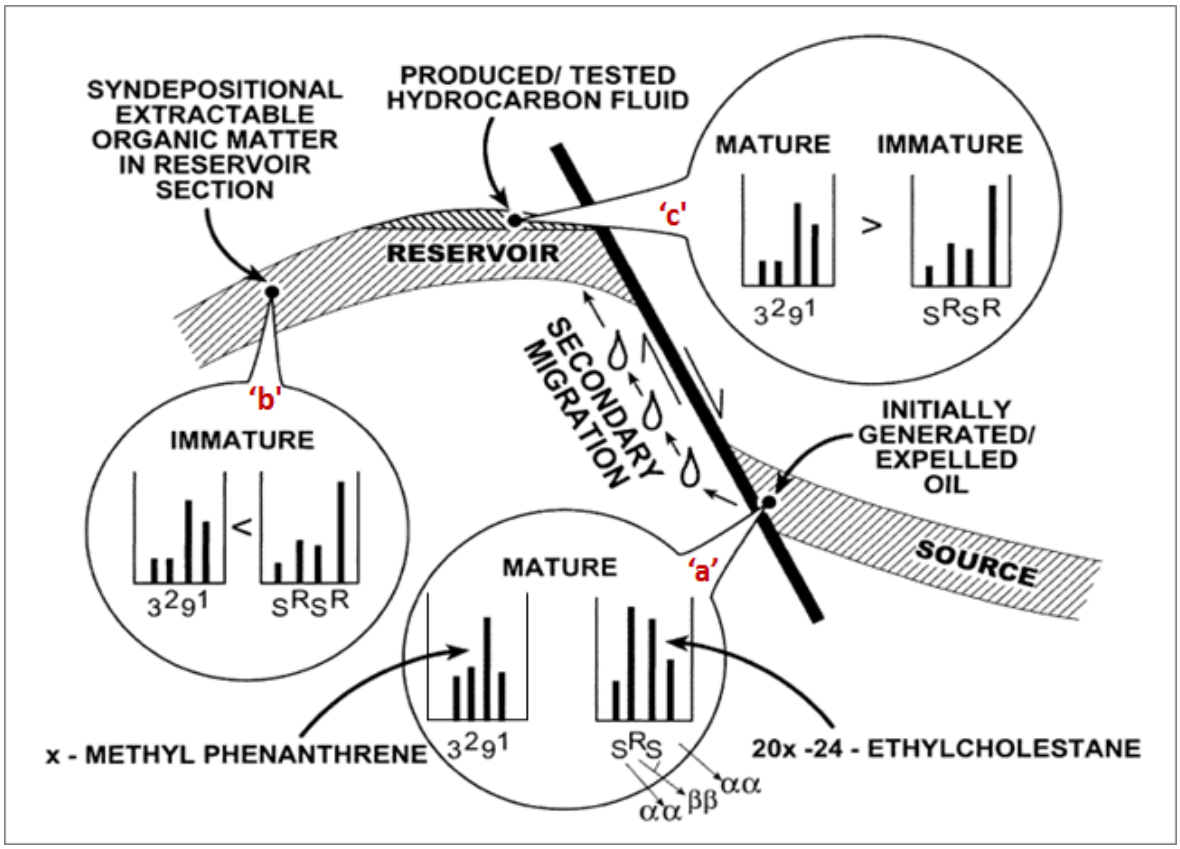


Figure 1.1 A typical migration scenario cartoon showing differences in maturity characteristics of migrating or produced petroleum due to migration-contamination. Migration occurs along a common fault, separating the source from the reservoir. Typical biomarker distributions are illustrated for (a) initially expelled oil; (b) the soluble organic matter in the host rock and; (c) the reservoired oil. '<' and '>' symbols show overall concentration differences. Note the disparity in the maturities of (a) and (b) and a maturity imbalance effects in (c) (after Curiale, 2002).

The application of regular biomarkers for understanding such complex processes as migration is known to be affected by other, equally important, geological factors such as thermal maturity of source rock and oils, source organic matter type and depositional

paleoenvironmental conditions (e.g. Trindade and Brassell, 1992). Also, interpretations based on many of these biomarkers are concentration-dependent and hence are affected by minor changes in these factors. Unsaturated hydrocarbons (olefins) and non-hydrocarbon compounds (e.g. carboxylic acids) are less routinely studied particularly due to their frequently very low concentrations in oils, and the often laborious procedures involved in their isolation and analysis (e.g. Jaffé *et al.*, 1988a, Curiale and Frolov, 1998, Jones *et al.*, 2001). On the other hand, it has been shown that these compounds can play a significant role in understanding petroleum origins and history, not only as biomarkers but also as indicators of migration-induced or in-reservoir alterations (Curiale, 1995). Because they generally occur in higher concentrations in immature and, perhaps, organic-rich sediments than petroleum itself, the imparting of an immature molecular characteristic to an oil having migrated through, or been reservoired in the former, is reasonable (Curiale, 1995, Hughes and Dzou, 1995, Curiale and Frolov, 1998). In addition, mature and effective source rocks of many of the world's largest Tertiary deltas have not been penetrated and are often not available for direct characterization (e.g. Li *et al.*, 2008), hence, the sometimes ambiguous, though well-known, approach to oil–source evaluation based on regular crude oil biomarkers alone, needs to be reconsidered.

Although numerous studies have been targeted towards demonstrating or substantiating already existing evidence of migration alteration by interpreting quantitative and qualitative data based on field petroleum samples, fewer studies have applied the use of the migration simulation approach to determine migration effects on crude oil composition. Furthermore, although reported simulation experiments have studied the concentration and distribution of well-known hydrocarbons (saturates and aromatics) over the past several decades (e.g. Chakhmakhchev *et al.*, 1982, Bonilla and Engel, 1986, 1988, Dieckmann, 1999), and more recently, a few non-hydrocarbon compounds such as carbazoles and phenols (e.g. Li *et al.*, 1995, Larter *et al.*, 1996, Clegg *et al.*, 1997, Lucach *et al.*, 2002) in crude oils, no study, to date, appears to have reported the migration-contamination effects on oil composition, using the abundance and distribution of olefins and carboxylic acids, in this manner.

This present study uses concentration data from petroleum olefins and carboxylic acids, supported by those of regular saturated and aromatic hydrocarbons, in various crude oils, from three geologically similar but geographically different petroleum producing regions of the world, to investigate the usefulness of these compound classes for detecting the occurrence of migration-contamination. These proposed migration-contamination markers are also compared with those in oil aliquots collected from laboratory simulated migration

experiments. This dual (field-laboratory simulation, and multi-biomarker) approach is aimed at providing a better understanding of the processes and factors that control petroleum migration-contamination in petroleum and how this can be gainfully applied in oil exploration studies.

1.2. Tertiary Deltas

The geographical settings and varied organic geochemical data of many Tertiary deltaic petroleum provinces have been well studied and described (e.g. Ekweozor *et al.*, 1979a, Hoffman *et al.*, 1984, Brooks, 1986a, Bustin, 1988, Thompson and Kennicutt II, 1990, Comet *et al.*, 1991, Magoon and Dow, 1994, Curiale, 1995, Snowdon *et al.*, 2004, Curiale *et al.*, 2005, Samuel *et al.*, 2009). A delta is formed by the deposition of deltaic facies (including both subaqueous and sub-aerial deposits) from river borne siliciclastic sediments into a standing body of water (e.g. Bustin, 1988, Magoon and Dow, 1994). Delta plains, mouth bars, inter-distributary bays, distributary channels, tidal ridges, prodelta muds etc., are eventually formed, as shown in Figure 1.2. These deposits and their distribution pattern are influenced by tidal, river, and wave forces, as well as gravity, and are transported in a manner to create a specific structure of reservoir sands. In all deltas, while the finest material is disseminated seaward, the coarser material is deposited at the mouth of the delta. Deltas are divided into an upper delta-, a lower delta- and a subaqueous delta plain (Samuel, 2008).

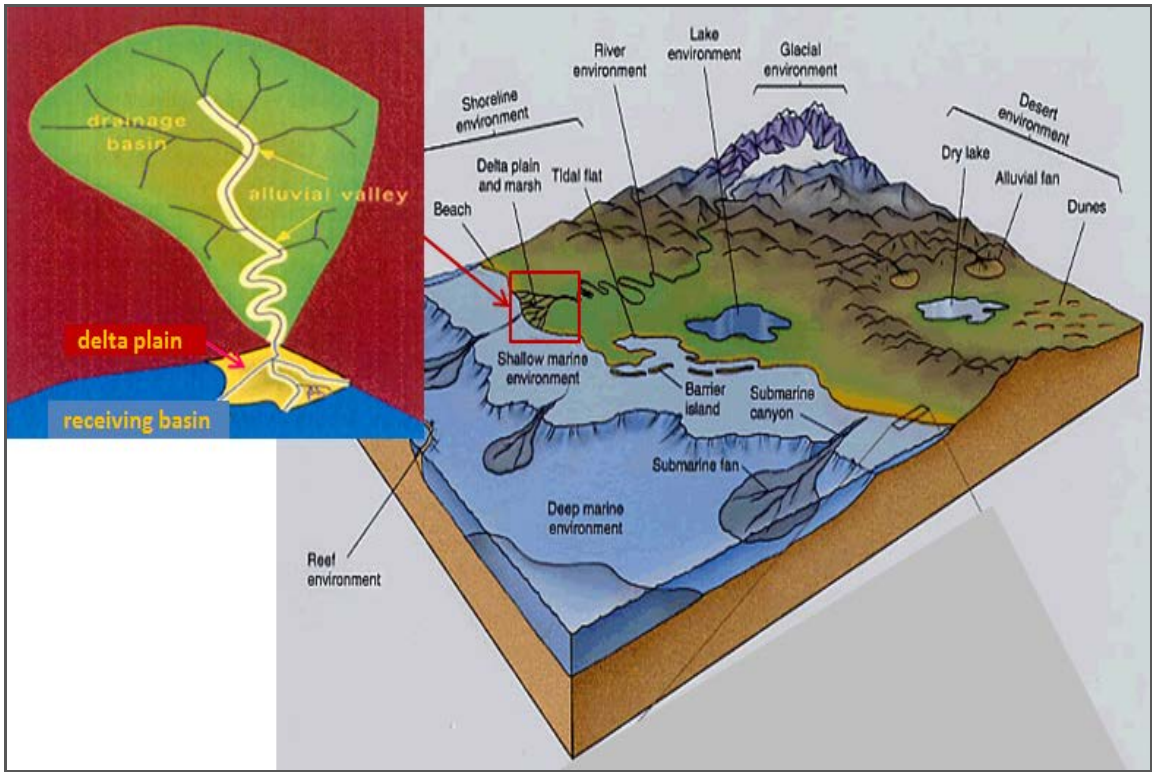


Figure 1.2 A schematic of various sedimentary depositional environments. The red square in the base figure highlights the deltaic setting among other environments (adapted from Samuel (2008) and http://academic.brooklyn.cuny.edu/geology/grocha/monument/images/deposit.gif).

Deltas are generally classified based on the collective influence of dominant processes: sedimentation process, waves and tide; and other variables such as climate, topography, coastal currents and tectonics of the receiving basin (Samuel *et al.*, 2009). The erratic and fluctuating impact of one or more of these factors have led to formation of various types of deltaic deposits including the most widely recognised 'Galloway' classification: fluvial-, wave- and tide-dominated deposits. Other types of classification are based on the Galloway's classification (Samuel, 2008, Chapter1, pp.41; and the references there in).

1.2.1. *Migration Drainage Style*

Deltaic petroleum provinces are considered to be closely associated with oil and gas pools within tens of kilometres of the source kitchen. Migration drainage in the delta features a combination of vertical and lateral migration (Todd *et al.*, 1997), and is determined from the structural and stratigraphic framework of the basin fill (Magoon and Dow, 1994). Lateral migration is fundamentally not an efficient process because of the lack of continuous carrier beds and, sometimes, the insufficient quantity of petroleum charge. The absence of continuous carriers is typically due to a poor permeability function controlled by basin lithostratigraphy and complexity (due to high degrees of faulting). Hence, lateral migration is more commonly restricted to distances of 20 km or less from the oil source (Ekweozor *et al.*, 1979b, Todd *et al.*, 1997). However, lateral migration has been found to predominate in certain instances especially where continuous seal-reservoir or carrier beds extend over a large area in a tectonically stable province (Magoon and Dow, 1994). On the other hand, vertical migration occurs, mainly up along active faults and fractures that breach a seal, and its connection to petroleum systems in rift basins and deltaic sequences. It could also be greatly enabled by the presence of hard formation overpressure in the source kitchen. Evidence of the incidence of overpressured zones in tertiary deltaic basins have been shown; Pearl River Mouth in China and Kutei in Indonesia are good examples (Oudin and Picard, 1982).

1.2.2. *Hydrocarbon Accumulation*

Modern deltas which are particularly dominated by river or tide are commonly the site of large hydrocarbon accumulations due to the contiguous positioning of characteristic rollover anticlines, and associated growth faults, to thick reservoir rocks (e.g. the Niger, the Mahakam, and the Mississippi; Ekweozor and Okoye, 1980, Comet *et al.*, 1991, Satyana *et al.*, 1999, Samuel *et al.*, 2009). The traps are commonly charged with hydrocarbons by a

more distal or underlying mature source rock (Magoon and Dow, 1994). The oil systems of Tertiary deltas, including Assam-Barail and Mahakam and Niger deltas are generally complex, and regardless of the huge petroleum accumulation in these basins our understanding of the pattern and the regional distribution of their source rocks within is lacking which may be partly due to the dominant charging style and lithostratigraphy of the basin (Samuel *et al.*, 2009, and the references therein). Establishing the dominant migration style in any deltaic basin is significant to predicting the location of petroleum occurrence in relation to the mature source rocks (Magoon and Dow, 1994, and the references therein).

1.2.3. *Deltaic Petroleum and Source Rocks*

A number of important evaluations have been published over the past few decades that highlight significant oil potential in deltaic settings, particularly in Tertiary coals (Powell and Boreham, 1994, Hunt, 1995, Davis *et al.*, 2007). Petroleum exploration has been extensively carried out in many deltas (e.g. Niger Delta and Kutei) without actually penetrating and sampling a significant source rock. Source rock characterisation in these areas has greatly relied on the geochemical characteristics of the associated oil (Ekweozor *et al.*, 1979a, Hoffman *et al.*, 1984, Sonibare *et al.*, 2008). Typical deltaic source rock lithologies are either shales or coals which contain predominantly higher land plant angiosperm input and, in some cases, some contribution of algal materials (Powell and Boreham, 1994). While commonly capable of expelling gas, coals are thought to be less commonly oil prone. This may be due to lack of certain conditions that are required for the realisation of an oil-prone coal. These factors are described in detail by Fleet and Scott (1994), and include: plant evolution, climate, preservation and transport mechanisms. Different types of data and parameter including microscopic, geochemical, petrographic, Rock-Eval hydrogen indices (HI), hydrocarbons and biomarkers etc. have been used, either separately or in an integrated manner, in attempts to obtain the best possible estimate and description of the oil potential of coals (Todd *et al.*, 1997), as well as possible prediction of their transport and deposition mechanisms (Davis *et al.*, 2007).

Several examples of characteristic selection of oil-prone coals from Tertiary basins in Indonesia have been documented. The source rocks in the Kutei Basin (Mahakam Delta) are the best and most widely described examples (Oudin and Picard, 1982, Hoffman *et al.*, 1984, Curiale *et al.*, 2005, Davis *et al.*, 2007), for their enrichment in coal-rich delta-plain facies. Another well documented example of oil-prone coals is that of the Ardjuna sub-basin of West Java which are concentrated in autochthonous delta plain coals (Noble *et al.*, 1991).

Evidence of yet another group of oil prone coals was illustrated by Todd *et al.* (1997) in their study report of Oligo-Miocene cores from the Balingian Province using geochemical data. In these and many other cases of coaly source rocks, a lower coastal plain environment is obvious from their sedimentology.

Deltaic petroleums are generally characterized by waxy oil (>10%), with high API gravity (~38-50), high Pr/Ph ratios (>3.0; Fleet and Scott, 1994), high hopane to sterane ratios, extended normal alkanes (>C_{34}), high C_{29} steranes and low to absent C_{30} 4-methyl steranes (due to limited marine source input), but are mostly low in asphaltenes and non-hydrocarbon (NSO) compounds (Powell and Boreham, 1994). Examples of some widely documented coal-derived oils include: crude oils of the Middle-Lower Jurassic coal measures in the Turpan Basin, China (Huang *et al.*, 1991); the Taranaki Basin in New Zealand which bears oil and gas sourced from coal and associated shales of the late Cretaceous to early Tertiary age (Czochanska *et al.*, 1988); oils of the Australian Gippsland, Cooper Eromanga and Bowen Surat Basins are also derived from terrigenous source rocks in which coal was a dominant component (e.g. Philp and Gilbert, 1986).

Tertiary oils of most Indonesian basins, especially the Kutei-Mahakam Delta, are predominantly sourced from Miocene terrigenous source rocks consisting of oil- and gas-prone interbedded coals and coaly shales (Todd *et al.*, 1997, Davis *et al.*, 2007, Doust and Noble, 2008); the Tertiary section of the Niger Delta has widely dispersed allochthonous terrigenous organic matter in fine grained and carbonaceous facies from which its oils are sourced (Ekweozor and Okoye, 1980, Bustin, 1988, Samuel *et al.*, 2009); the Beaufort-Mackenzie Basin, like the Niger delta, also consists largely of a Tertiary delta in which allochthonous terrigenous organic matter appears to be the source of oil in this basin, e.g. the Eocene-Palaeocene Richard Formation, believed to be the main source rock, is derived from Carboniferous species (Brooks, 1986a, Curiale, 1991, Snowdon, 1991, Li *et al.*, 2008); Jurassic coals of the Norwegian section of the North Sea are thought to be the major source for oil in the Haltenbanken region (Forbes *et al.*, 1991). However, establishing a genetic relationship among the oils and supposed source rocks in many of these Tertiary deltaic basins remains unclear due to the complexity of the deltaic basins structure (Doust and Sumner, 2007, Samuel *et al.*, 2009).

1.3.The Petroleum System Concept

According to Magoon and Dow (1994), a petroleum system is an assembly of all necessary elements and processes that must be present within a known period for a hydrocarbon

accumulation to exist. In other words, it represents the natural context through which all related hydrocarbon deposits are linked by origin and occurrence (Doust and Sumner, 2007). These geologic elements and events include petroleum source-, reservoir-, seal-, and over burden rock, generation, expulsion, secondary migration, accumulation and retention, which must occur in time and space so that source organic matter can be converted to recoverable petroleum (Magoon and Dow, 1994). Petroleum systems are described based on an extensive, reliable database of geochemical data of oil and gas traces, as well as detailed geological and geophysical data. Both detailed accounts and overviews of these petroleum systems have been documented and continually reviewed over the years (Davis *et al.*, 2007). However, the demonstration of the concept by Magoon and Dow (1994) has steered efforts towards improved approach to group various petroleum systems (e.g. Figure 1.3).

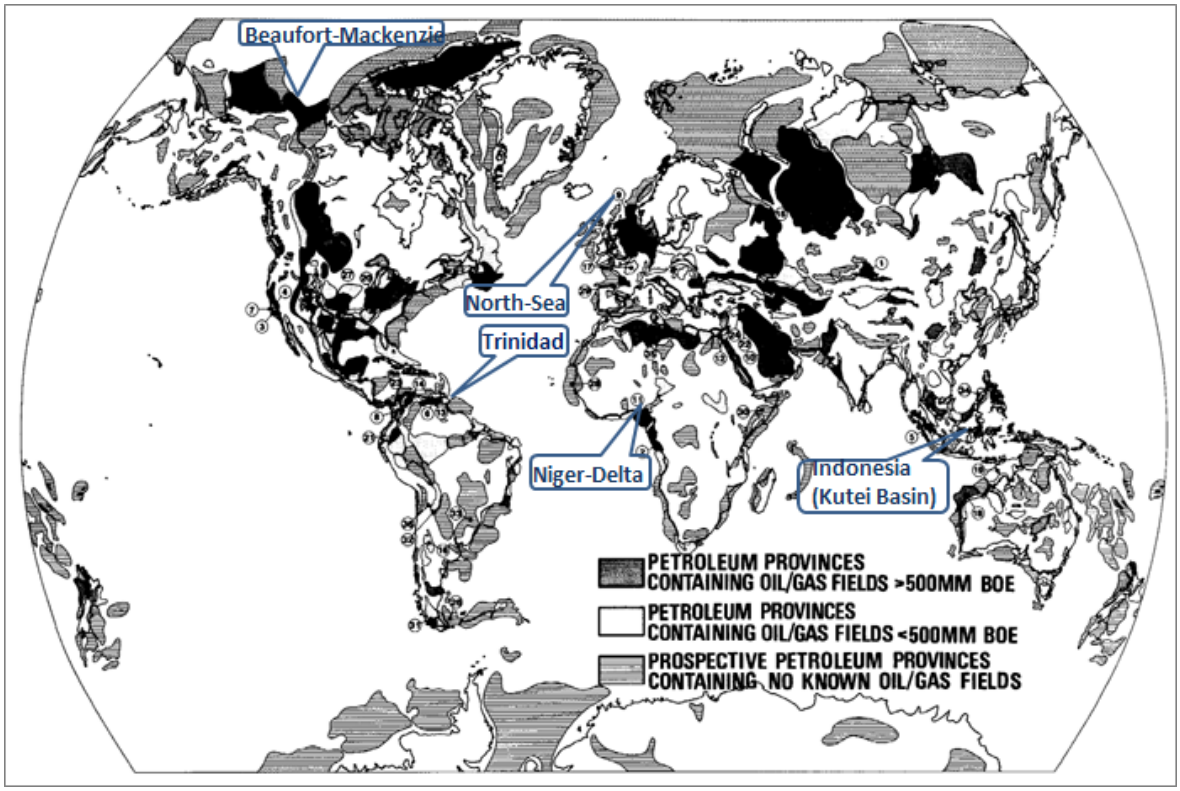


Figure 1.3 Map of the world petroleum provinces showing oil and gas fields of varying capacities based on the presence of a source rock, and prospects for oil and gas; but some may still be unproductive. The highlighted areas are indicate sources of the study samples. BOE is Barrel of Oil Equivalent (adapted after Demaison and Huizinga, 1994).

The concept and study of petroleum systems is significant in establishing a genetic relationship between an active mature source rock and the associated hydrocarbon accumulation. It also provides a robust link between oil and gas distribution and structural evolution of a basin (Ekweozor and Daukoru, 1994, Magoon and Dow, 1994, Doust and Sumner, 2007). The concept is limited in application to certain basins due to localization, as opposed to dominance and consistency, of characteristic lithofacies. Examples of basins that fall into this category are most Tertiary Indonesian (syn-rift and post-rift) deltaic basins

which are typically dominated by suites of indigenous lithologies. This complexity has been shown to be responsible for the difficulty in establishing a definite source-rock-reservoir-seal relationship, as well as accurate oil-source correlation assessments (Curiale, 2008, Doust and Noble, 2008).

1.4. Overview of Case Study Deltaic Basins

Many anomalous oil assessment results with associated unusual biomarker distributions have been observed to occur, mostly, in many oils of the Tertiary/deltaic systems, as evidenced in literature (e.g. Philp and Gilbert, 1986, Jaffé *et al.*, 1988b, Ukpabio *et al.*, 1994, Curiale, 2002). These oils have typically migrated through organic-rich, thermally immature faulted rocks or carrier beds. In the present study, twenty-nine deltaic oil samples were investigated. These were selected from various oil fields of three major, extensively studied and predominantly Tertiary deltaic systems. The aim was to obtain a global representation of this geological setting which is reported to favour the conditions needed for this migration-contamination phenomenon to occur. This section, therefore gives a general description of each of these three Tertiary deltaic regions from which the oils that make up the suite of field samples examined in this study were obtained. Table 1.1 summarises the geologic and geochemical characteristics of these crude oils.

Table 1.1 Summary of the petroleum geology and geochemistry of case study petroleum-producing Tertiary deltas. (!) Denotes a known petroleum system, while (.) is used to refer to a hypothetical petroleum system type (PST).

Basin/ Province	Dominant source rock type	Age of source rock	Main reservoir/ overlying seal	Principal maturation stage	Petroleum system type- PST/ origin/ charge	Main produced HC	References
Beaufort/ Mackenzie	Pre-Tertiary-Tertiary deltaic shale- Type II/III 'resinitic'? source rocks, with mainly land plant input.	Eocene-Palaeocene (Upper Cretaceous - Tertiary).	Neogene deltaic sandstones with overlying shaly formations.	Late Tertiary – Recent; R_0 max ≤ 0.7.	Tertiary and Cretaceous (mixed) systems; Extensive vertical migration.	Oil and condensate	(Lane and Jackson (1980), Snowdon and Powell (1982), Brooks (1986a), Powell and Boreham (1994))
Kutei (Mahakam Delta)	Type II/III deltaic/paralic coals/mudstones & carbonaceous shales; OM is dominantly land plant-derived.	Mid-Late Miocene.	Regressive deltaic, coastal plain, & marine turbidite? Sandstones/ regional marine shales.	Mid Miocene – Recent; Various HC generative thresholds: R_0 = 0.35-0.6; 0.6-1.2; ≥ 1.2.	Late post-rift regressive deltaic (!) PST4; oil migration is largely lateral; Source rocks are contiguous with sandstone reservoirs.	Oil and gas (mainly gas).	(Oudin and Picard (1982), Powell and Boreham (1994), Todd *et al.* (1997), Davis *et al.* (2007), Doust and Noble, 2008); Curiale *et al.* (2005)
Niger Delta	Marine/coaly shales of Akata /Agbada Fm; mixed kerogen (II-III), but mainly humic, Type III; OM is mainly land plant-derived.	L.Cretaceous –Tertiary.	Neogene Agbada deltaic sandstones overlain by marine clays of Benin Fm.	Late Tertiary– Recent; R_0 = 0.2-0.8.	Akata-Agbada(.); various but principally Tertiary deltaic (!) PST; source and reservoir units are superimposed; Migration is dominantly vertical (short, updip).	Oil and gas.	(Ekweozor and Okoye (1980), Bustin (1988), Haack *et al.* (2000), Sonibare *et al.* (2008), Samuel *et al.* (2009))

1.4.1. *Beaufort-Mackenzie Basin*

The Beaufort–Mackenzie Basin in Arctic Canada (Figure 1.4) is a petroliferous province still in the early stages of exploration. It is one of three major tectonic features of the Mackenzie Delta region in northwest Canada (Cook *et al.*, 1987), formed by thick succession of Upper Cretaceous-Cenozoic sediments prograding northward across the continental margin adjacent to the oceanic Canada Basin (Snowdon and Powell, 1982, Curiale, 1991, Li *et al.*, 2008). The deposition took place during either the Pre-Cretaceous continental rifting or final stages of Tertiary orogenesis and most gas and oil discoveries are trapped in these resulting extensional structures (Dixon *et al.*, 1992). The thick sequence (12-15 km) consists of irregularly folded and faulted deltaic complexes deposited as Tertiary Moose Channel, Reindeer (mudstones and sandstones), Richards, Kugmallit (marine and non-marine sands and mudstone), and Mackenzie Bay and Beaufort Formations (Curiale, 1991). These are bounded by listric normal faults on the south edge of the Beaufort-Mackenzie Basin (Cook *et al.*, 1987). A generalized stratigraphic framework and classification in the Beaufort-Mackenzie Basin are shown in Figure 1.4.

Resources for the Mackenzie Delta-Beaufort region are estimated at 9 billion barrels of oil and 112 trillion cubic ft. of gas, with recoverable reserves in the Canadian Beaufort alone of about 1.5 - 2 billion barrels of oil and 12 trillion cubic feet of natural gas. The Mackenzie River Delta is host to Amauligak, the biggest offshore field discovery with estimated reserves of over 1billion barrels of oil (Curiale, 1991). To date, over 50 significant oil and/or gas field discoveries, some of which are shown in Figure 1.5, have been made in this significant hydrocarbon province (Curiale, 1991, Lane, 2002). The tectonic history and evolution of this region plays a vital role in establishing this oil and gas potential. Normal faults are developed beneath the Mackenzie Delta and Tuktoyaktuk Peninsula from where petroleum migration is believed to occur into the shallower folds and secondary faults. The oil and gas discoveries beneath the Delta, in the central Beaufort, and at Amauligak are good examples of significant accumulations (Lane, 2002). Considerable volumes of oil and gas have been discovered in Tertiary rocks, principally in Eocene and Oligocene delta-front strata, with lesser volumes in Paleocene and Miocene strata (Dixon *et al.*, 1992). The Beaufort-Mackenzie Basin is generally characterized by extensive vertically-drained petroleum systems with expected oil-mixing and/or migration-contamination effects (Li *et al.*, 2006, Li *et al.*, 2008).

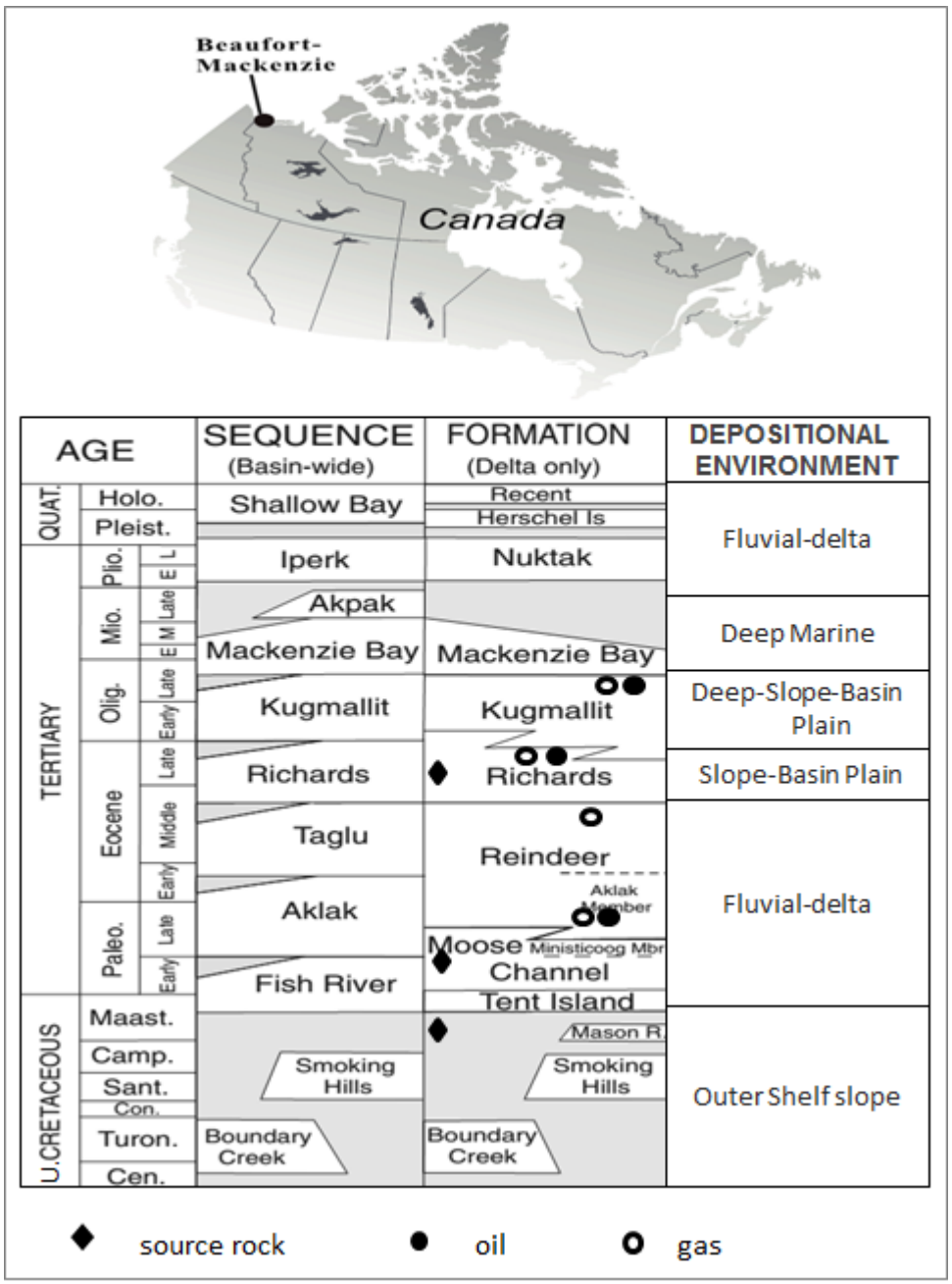


Figure 1.4 Location map and generalized stratigraphic chart showing the names of formation and sequence, and their depositional environments, for the Beaufort–Mackenzie Basin (modified from Tang and Lerche, 1992, Snowdon *et al.*, 2004, Li *et al.*, 2008).

Over the past two decades, extensive geochemical efforts have been made in the assessment of source units of the Beaufort-Mackenzie Delta (Lane and Jackson, 1980, Snowdon, 1980, Brooks, 1986a, Brooks, 1986b, Curiale, 1991, Snowdon *et al.*, 2004, Li *et al.*, 2006, Li *et al.*, 2008). Detailed studies have since been carried out on various geological and geochemical aspects of the basin by many researchers including, the concept of early generation and expulsion (e.g. Snowdon and Powell, 1982, Hunt, 1995); source rock attributes and maturity (e.g. Snowdon and Powell, 1979) and general detailed biomarker studies (e.g. Brooks, 1986a, Li *et al.*, 2006, Li *et al.*, 2008). Most of these published reports on the source rock potential and crude oil geochemistry of the Canadian Beaufort and

Mackenzie Delta have generally grouped the Tertiary oils into two main genetic families: Tertiary- and Cretaceous-sourced (Curiale, 1991, and the references therein). The biomarker content of Tertiary oils and source rocks from the offshore Beaufort-Mackenzie Delta suggest a terrestrial origin with predominant land plant contribution to the source. This is evidenced by the widespread abundance of 18α(H)-oleanane, a major triterpane and source-specific marker of the oils, which have been observed to correlate, in concentration, with lupanes, if separated, in individual oils (Brooks, 1986a). This relationship is the consequence of their related origins and the collective concentration reduction effect of increasing maturity on these biomarkers (Brooks, 1986b, Snowdon *et al.*, 2004). Although lupanes are not assessed in this study, previous workers have shown that these compounds can be successfully separated by using a polar GC-column or reverse phase HPLC (Nytoft *et al.*, 2002, Peters *et al.*, 2005).

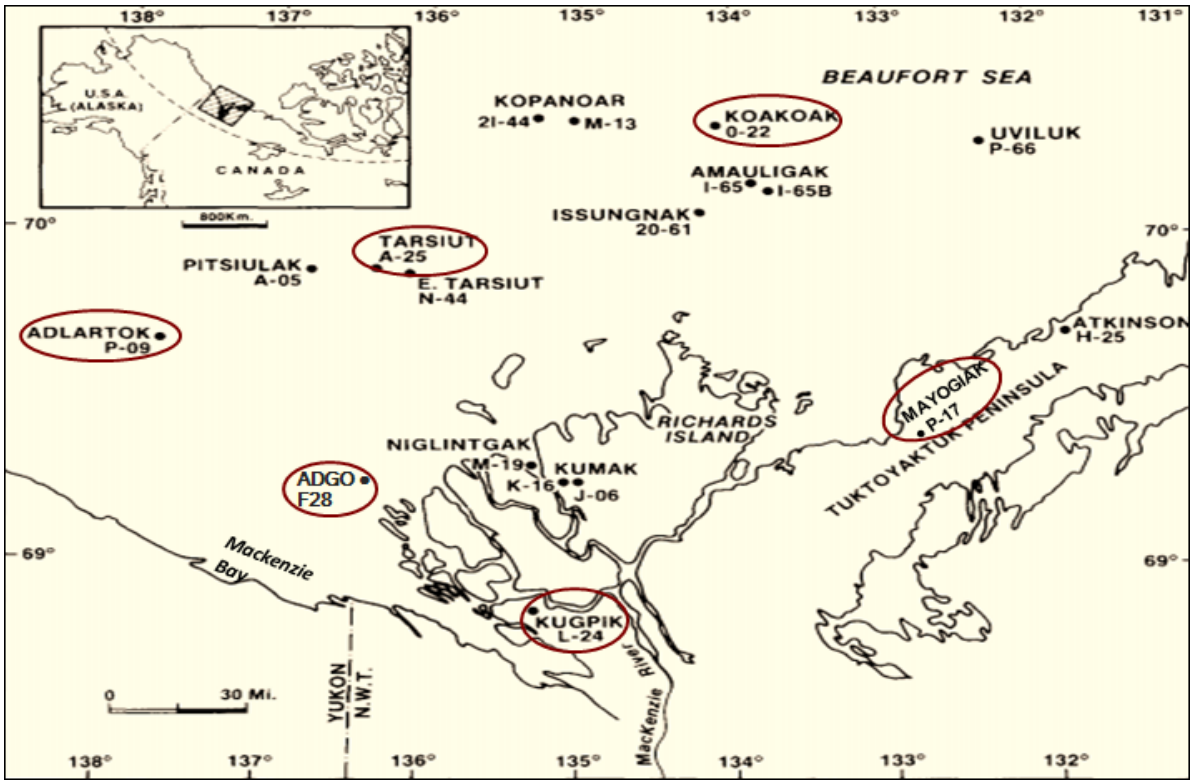


Figure 1.5 Location map (inset) for Canadian Beaufort and Mackenzie River Delta in the Northwest of Canada showing some of over 50 significant oil and gas discoveries, including sources (red-circled) of case study oil (adapted from Curiale, 1991).

The Tertiary hydrocarbons of the Beaufort–Mackenzie range in maturity from extremely immature to moderately mature (Brooks, 1986a). The possibility of early generation of unusually low thermal maturity oils in Mackenzie Delta sediments (VR ≤ 0.6%Ro), using standard maturity indicators and other biomarker parameters, has been shown and discussed (Snowdon and Powell, 1982). Although recently suggested, by some workers, as rather, the consequence of migration-contamination, than maturity at expulsion (Li *et al.*, 2006, Li *et*

al., 2008), it has been previously proposed, based on experimental data, that the source of early generated immature oil and condensates in the region were the immature source rocks consisting of conifer-derived allochthonous, terrigenous, resinitic-type organic matter (Snowdon, 1980). Various explanations for the proposal and subsequent evolution of the resinite hypothesis have been given in more detail (Snowdon, 1991). This is mostly due to a number of 'unusual' observations in several geologic specimens of the Beaufort-Mackenzie delta. More significantly, the unusual composition and characteristics of the oils and occurrence of resin-derived markers in other terrigenous oils are all indicative of higher plant resins as major sources of petroleum hydrocarbons in the region (Powell and Boreham, 1994).

As with many other Tertiary deltaic basins (e.g. Niger Delta), the deeper effective source rock volumes have neither been penetrated, sampled nor evaluated (Li *et al.*, 2006), hence, difficulty identifying adequate source rock characteristics in the Beaufort-Mackenzie sequence has led to attempts at inferring these attributes through the characterization of associated oils. Despite the lack of a clear geologic indication for the origin of these Tertiary oils, a Paleogene source (Kugmallit/ Richards/Reindeer) is mostly preferred (Curiale, 1991; and the references therein). This view agrees with previous studies such as those by Brooks (1986a; 1986b) in which the Eocene-Palaeocene Richards Formation was proposed as the effective source rock, using oil-source correlation data. However, Curiale (1991) presented a supporting conditional evidence for a Mid-Upper Paleogene source for the Tertiary oils of the Canadian Beaufort based on the occurrence of the large Amauligak deposits within the thick Kugmallit sequence, overlying the thickest part of Richards Formation. The Beaufort-Mackenzie deltaic source rock appear to have higher concentrations of organic resinites than other Tertiary deltas; and this mostly accounts for the preferential generation of predominantly naphthenic-aromatic oils rather than the paraffinic type in this area (Powell and Boreham, 1994; and references therein).

1.4.2. *Kutei Basin (Mahakam Delta)*

The Kutei Basin is a highly prolific Tertiary sedimentary basin located in eastern Kalimantan. Kalimantan is the Indonesian portion of the island of Borneo, covering a significant area of the island. The 60000 km^2 Kutei Basin is the largest (165,000 km^2) and deepest (12-15 km) basin in Indonesian petroleum province (Moss *et al.*, 1997, Moss and Chambers, 1999, Satyana *et al.*, 1999). Being an actively exploited sequence at the present, the delta is also one of the richest, with reserves totalling more than 3.5 billion barrels of oil

and 35 trillion cubic feet of gas, which led to increasing production into the deep water parts of the basin within the last two decades (Moss and Chambers, 1999, Curiale *et al.*, 2005, Davis *et al.*, 2007).

It is bounded to the north by the Mangkalihat High; hinges, to the south, on the Adang-Flexure; terminated by the Kuching High-part of the Kalimantan Central Ranges to the west; and opens into the Makassar Strait to the east as shown on the map in Figure 1.6 (Satyana *et al.*, 1999). The Tertiary depositional history of the Kutei Basin includes an Early Synrift, alluvial; Late Synrift, deep marine; Early Postrift, deep marine (carbonate and clastic); and Late Postrift, deltaic to deeper marine. Only the Late Postrift contributes to the dominant petroleum geology of the Kutei Basin (Moss and Chambers, 1999, Doust and Noble, 2008). Deltaic deposition continues today in the form of the present-day Mahakam Delta. Based on its Tertiary evolution, the basin may be sectioned into two sub-basins namely, a western (Inner or Upper) and an eastern (Outer or Lower) Kutei Basins (Figure 1.6). The eastern (outer-lower) part of the Kutei Basin is a major oil and gas area hosting a high concentration of the giant producing oil and gas fields in the basin, all of which occur in the Samarinda Anticlinorium-Mahakam Fold-belt (Moss *et al.*, 1997, Satyana *et al.*, 1999). Here, the distribution of oil and gas fields is thought to primarily depend on the relative positions of the hydrocarbon generation and the overpressured zone (Oudin and Picard, 1982, Todd *et al.*, 1997).

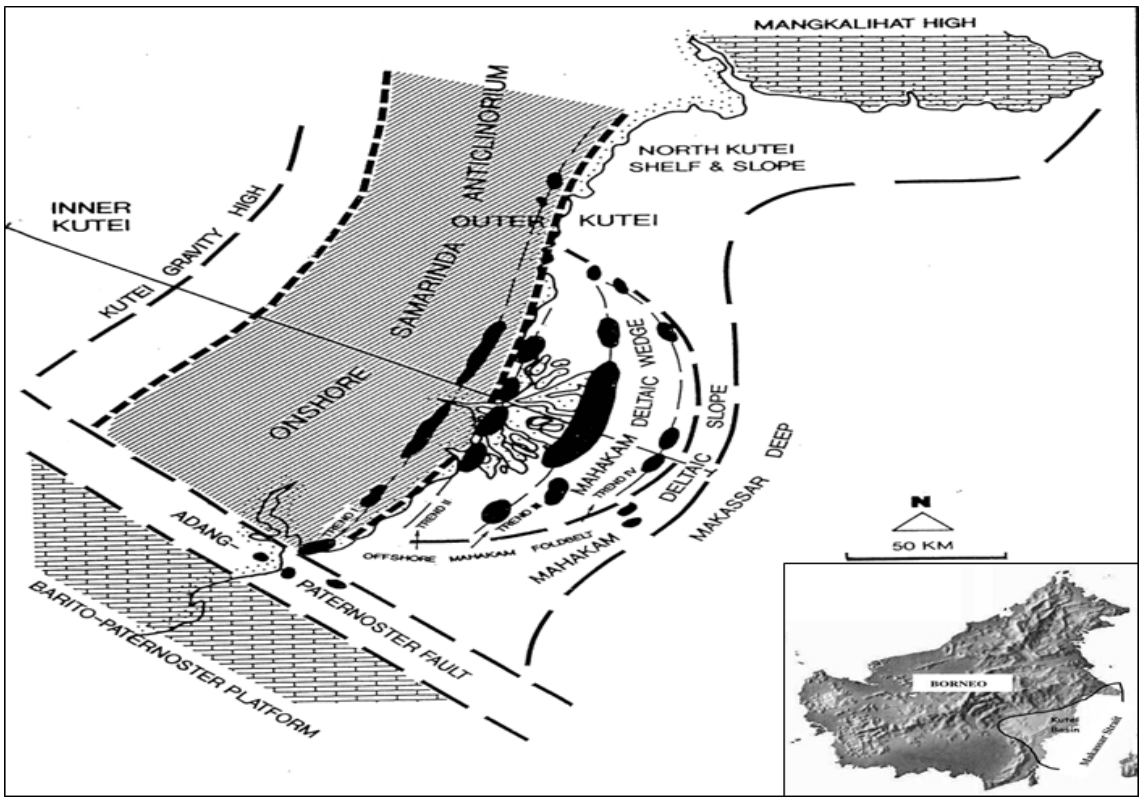


Figure 1.6 Physiographic and tectonic map of the Kutei Basin, East Kalimantan showing producing fields. The inset shows the position and approximate outline of the basin within the island of Borneo (adapted from Satyana *et al.*, 1999, and Curiale *et al.*, 2005).

The nature and geochemistry of hydrocarbons and source rocks of Kutei Basin have been reviewed and described by many authors (e.g. Hoffman *et al.*, 1984, Moss *et al.*, 1997, Todd *et al.*, 1997 , Moss and Chambers, 1999, Satyana *et al.*, 1999, Curiale *et al.*, 2005, Davis *et al.*, 2007, Doust and Noble, 2008), and they generally agreed that the host organic matter in form of kerogen is dominantly of terrigenous (land plant) Type II-III origin, but may contain some algal-lacustrine input derived from floodplain lakes (Figure 1.7). This could be due to efficient removal of resulting detritus, of extremely rapid tropical plant growth on Borneo, by the Mahakam River and its tributaries. The effective source rock potential is enhanced by elevated heat flows and geothermal gradients in several parts of the basin (Curiale *et al.*, 2005, and the references therein). The dominant source rock depositional environment in the Kutei Basin is paralic or deltaic and has been described in detail by Todd *et al.* (1997). Briefly, hydrocarbons from this type of source rock arise from coals and coaly shales deposited in a variety of fluvial to coastal plain environments. In general, these coaly source rocks, with associated carbonaceous and clastic shales generate a mixture of oil and gas (Satyana *et al.*, 1999, Doust and Noble, 2008).

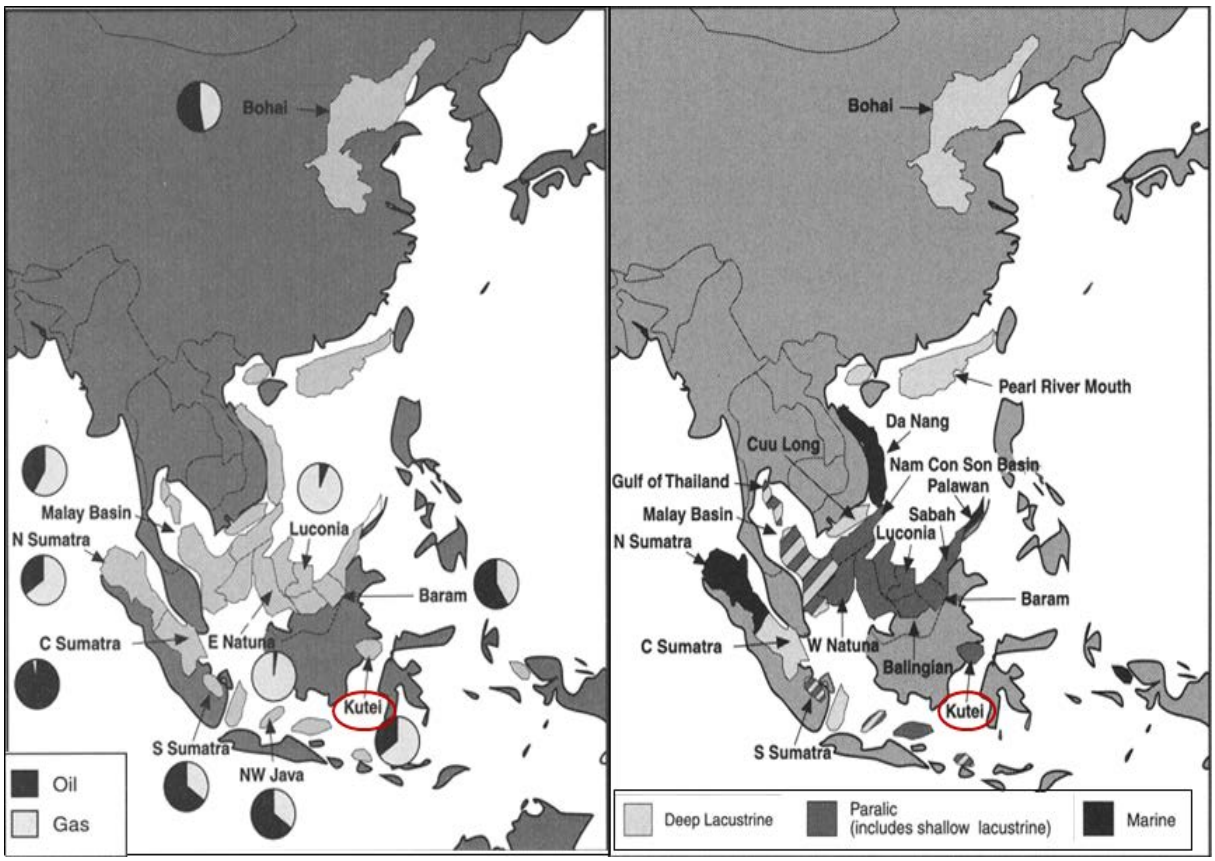


Figure 1.7 Location maps of the of Kutei basin among major South-East Asian oil provinces showing approximate proportions of different petroleum (oil and gas) types and its principal source type (after Todd *et al.*, 1997). Note the distribution and proportion of oil/gas in the Kutei oils. Source rock type is paralic, with some lacustrine input.

Kutei hydrocarbons are reservoired overwhelmingly in the Miocene deltaic sands of the Balikpapan (Middle Miocene) Formation. Migration has occurred laterally up dip to a maximum distance of 10 km to accumulate in anticlinal traps. Based on numerous reported geochemical data, most of the Kutei oils are found above the "oil-mature zone", a likely indication of occurrence of an upward migration of oil above its zone of generation (Oudin and Picard, 1982 and the references there in). They are typically characterized as land plant-derived, with high wax content, low sulphur and elevated pristane/phytane ratios (Satyana *et al.*, 1999). Numerous petroleum system (and subsystems) types (PST) have been suggested and recognized in the Kutei Basin (Mahakam Delta) including the undeveloped Tanjung–Berai(.); the marine Klinjau–Klinjau(.) and Tanjung–Kutei(.) PST3; a recently discovered deep-water Miocene-Mio/Pliocene(.), and an overwhelmingly dominant late post-rift regressive deltaic Balikpapan-Balikpapan(!) PST4. The notations in parentheses are used to refer to undeveloped, non-productive, potential, or hypothetical (.) PSTs, and well-known, dominant, or prolific (!) PSTs, correspondingly. The late post-rift regressive deltaic PST4, described in detail by Doust and Sumner (2007) and Doust and Noble (2008), is the only developed system in the Borneo basins family to which Kutei–Mahakam belongs.

However, this list is subject to constant reviews at any time, following further and continuous geochemical studies on this basin.

1.4.3. *The Niger Delta*

The Niger Delta ranks among the world's most prolific and largest hydrocarbon-producing Tertiary deltas. It is located in southern Nigeria at the north eastern continental margin of the Gulf of Guinea on the west central coast of Africa (Figure 1.8). It covers a catchment area of over one million square kilometres of savannah lowlands, and a sub-aerial extent of at least 75000 km^2 (Ekweozor and Udo, 1988, Doust, 1989, Sonibare *et al.*, 2008, Samuel *et al.*, 2009). The basin has many discovered fields (481 oil and 93 natural gas fields) with proven ultimate recovery of well over $4x10^9$ $m^3$of oil (Doust, 1989) and over 2.7 trillion cubic meter of gas, with an estimated reserve of about 23 billion barrels of oil and 183 trillion cubic feet of natural gas (Sonibare *et al.*, 2008).

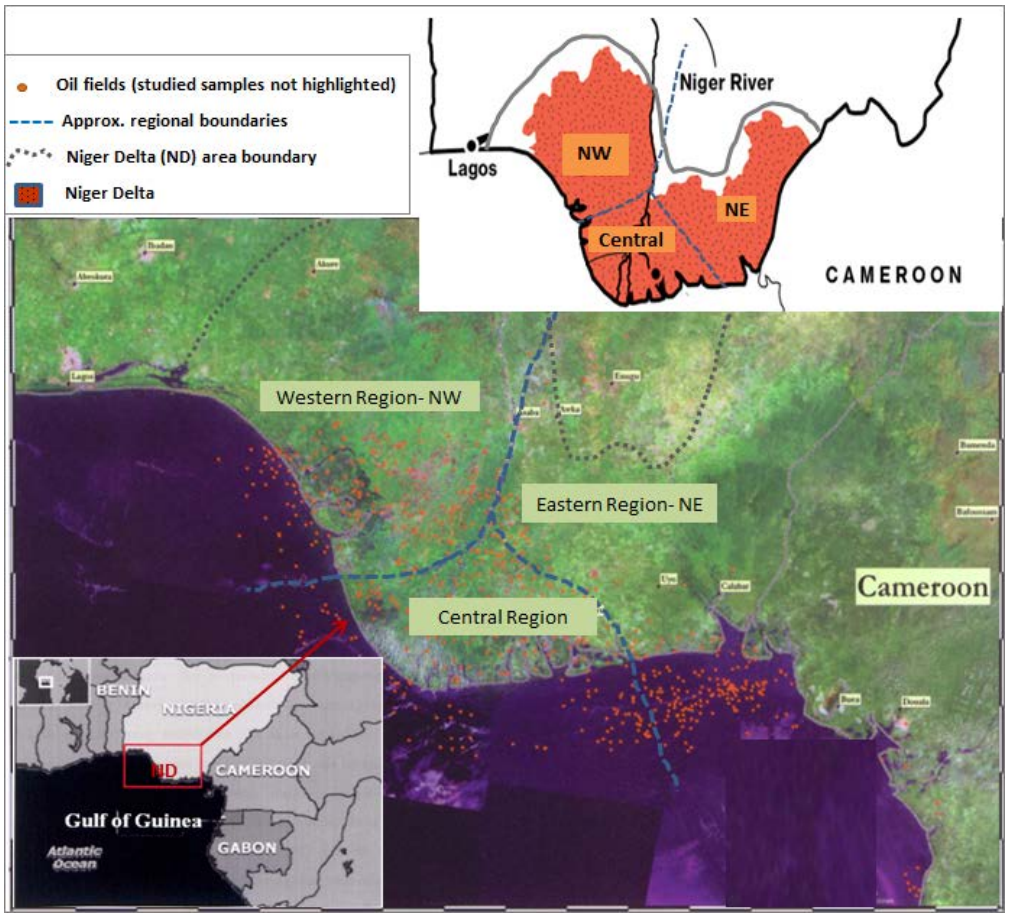


Figure 1.8 Geological map showing the location of the Niger Delta 'ND' in the south western Nigeria coast as indicated in the topmost enlarged area, and showing the three regions (NW, NE & Central) of the delta in which the oils are grouped. The inset shows the position of the ND/Nigeria within West Africa and the Gulf of Guinea. The orange spots indicate produced oil and gas fields, study sites are not highlighted. The ND is one of the world's largest, covering a sub-area of about 75000 km^2 (adapted from Mitchell, 2006, and Samuel, 2008).

The Niger Delta was formed at the point where the mouth of the Niger, Benue and Cross River drainage systems (Benue Trough) adjoined the central Atlantic Ocean during the increased influx of Niger River clastics from the adjacent highlands in the early Tertiary (Doust, 1989, Samuel *et al.*, 2009). It consists of a regressive clastic (deltaic and marine) sedimentary sequence of about 9-12 km thick (Doust, 1989, Sonibare *et al.*, 2008). The sedimentary sequence of the Tertiary Niger Delta, as shown in Figure 1.9, is generally thought to consist of three superimposed lithostratigraphic units: the Akata, Agbada and the Benin formations, corresponding to three depositional environments namely, marine, intermediate (mixed marine and terrigenous) and terrigenous respectively (Weber, 1971, Ekweozor *et al.*, 1979a, Ekweozor and Udo, 1988, Ukpabio *et al.*, 1994, Samuel *et al.*, 2009). The depositional conditions and features of these lithofacies are summarised in Table 1.2.

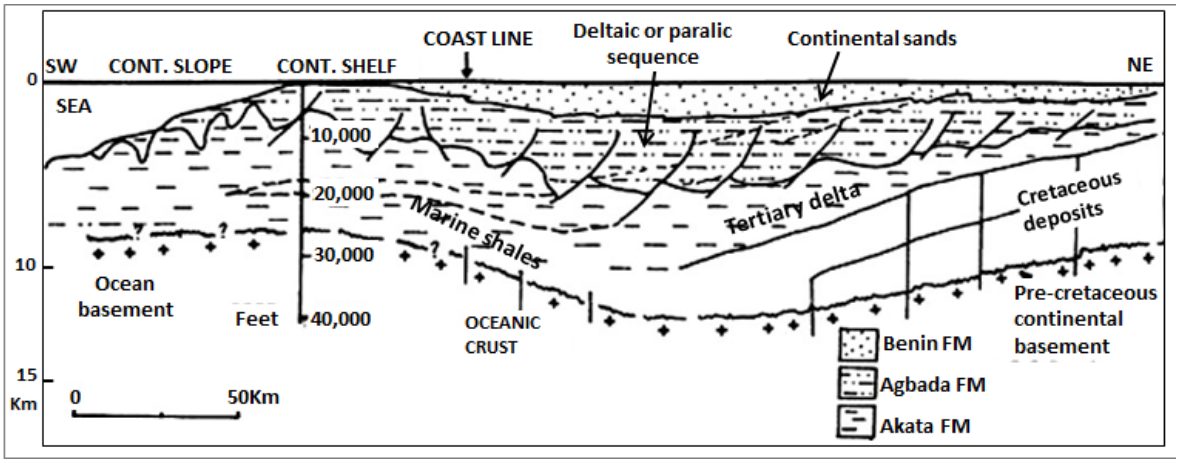


Figure 1.9 A schematic section across the coastline showing the stratigraphy of the Niger Delta. The delta sequence consists of Tertiary sediments of up to 12 km thick. Here, a regressive cycle is formed in which 3 basic lithostratigraphic units are developed: Akata-Marine, Agbada-Deltaic/paralic sands and shales, and Benin-alluvial or continental sands (adapted from Weber, 1971, Doust, 1989, and Ukpabio *et al.*, 1994).

Many aspects of the sedimentary organic matter and oils of the Niger Delta have been studied extensively by several workers over the past four decades (Weber, 1971, Ekweozor *et al.*, 1979a, Bustin, 1988, Doust, 1989, Ekweozor and Daukoru, 1994, Ukpabio *et al.*, 1994, Haack *et al.*, 2000, Eneogwe and Ekundayo, 2003, Sonibare *et al.*, 2008, Samuel *et al.*, 2009). The findings of these studies agree that the organic matter source type is mainly a mixture of Types II and III kerogen, geochemically similar for both the Akata and Agbada shales, and is thought to be oil and gas prone. More importantly, the organic matter is widely distributed throughout the stratigraphic sequence. The geochemistry, petrology and distribution data of the organofacies indicate a predominantly terrestrial and detrital source input, and this is linked to the age of the strata and depositional environment. These studies have also observed that the Niger Delta hydrocarbons reside mostly within the sandstone pockets of thousands of individual reservoirs within oil-rich shale strata of the Agbada

Formation where they are usually trapped in rollover structures associated with paralic interval growth faults. These growth faults, as indicated by some of the studies, form vertical conduits connecting successive reservoirs which are widely spaced in depth in most of the fields, and ranges from 10 to 20 km in thickness, and are Eocene to Pliocene in age (e.g. Weber, 1971, Weber *et al.*, 1978).

Table 1.2 Summary of the lithology and stratigraphy of the Niger Delta (Ekweozor *et al.*, 1979a, Ekweozor and Daukoru, 1994, Sonibare *et al.*, 2008, Samuel *et al.*, 2009).

Lithofacies/ formation	Age range	Sedimentary thickness (m)	Depositional conditions & features
Akata	Paleocene - Miocene	600 – 6000 (delta margin – central onshore)	Marine; basal overpressured marine shale, of prodeltaic facies deposited in deepwater under anoxia
Agbada	Eocene-Miocene	300 - ≥4000 (delta margin – central onshore)	Intermediate: paralic sequence of alternating, interbedded sands and shales deposited in shallow waters
Benin	L. Eocene - Recent	Up to 2000 (delta margin – central onshore)	Continental: mainly fluviatile alluvium and sandstones deposited in fluvial and coastal environment

The hydrocarbon source rocks, aged between Late Cretaceous and Tertiary, are both in the lower parts of the paralic sequence of the Agbada Formation and the uppermost strata of the continuous marine shales of the Akata Formation (Weber, 1971, Ekweozor *et al.*, 1979a, Sonibare *et al.*, 2008 and the references therein), which are presumed to be the common source for all the oils of the Niger Delta based on positive oil-source rock correlations (Doust, 1989, Ekweozor and Daukoru, 1994). The Niger Delta type of source rocks are endowed with volume, excellent migration routes due to the presence of interbedded permeable sands, and a relatively rapid maturation rate (Bustin, 1988). Hydrocarbon accumulations are believed to have resulted from the petroleum migration within short upward distances from the mature facies and by long-range vertical migration via growth faults from the deep Akata shale to the shallow reservoirs sands in the Agbada Formation (Ekweozor *et al.*, 1979b).

Although no consensus has yet been reached as to the effective petroleum system(s) in the Niger Delta Basin, many workers have made some proposals in this regard. The latest recommendations have generally been based on studies of source rocks in basins marginal to the delta, and are apparently unrepresentative (Samuel *et al.*, 2009; and the references therein). One such classification was proposed based on available geochemical data, and includes, a Lower Cretaceous system, characterized by lacustrine source rocks; an Upper

Cretaceous-Lower Palaeocene system, characterized by marine source rocks; and a Tertiary petroleum system, comprising source rocks of Types II-III kerogen and encompassing the entire delta including the deep-water areas (Haack *et al.*, 2000). A somewhat similar source input/deposition-type classification was later proposed by Eneogwe and Ekundayo (2003), and comprised of a significantly onshore marine system; a near offshore mixed marine/terrestrial system; and a predominantly further offshore terrestrial system. However, in their in-depth revision of the Niger Delta petroleum systems, Samuel *et al.* (2009) pointed out that only the Tertiary delta/terrestrial (Akata-Agbada) petroleum system correlates at molecular level with a good number of the delta's shallow water oil deposits. They (Samuel *et al.*, 2009) argued that the other implied systems remain hypothetical until proven otherwise, since the basis for their inference is insubstantial.

1.5.Research Questions and Hypotheses

The reflection of weak correlation between many produced oils and their source rocks within Tertiary deltaic systems appears to be a widespread phenomenon and this has raised some key questions such as: why is this peculiar to major Tertiary deltaic systems; and which post-generation (migration and in-reservoir) process mechanism, if it exists, could be contributing significantly to changes in initial composition of these oils, thus making oil-source rock correlations so challenging? On reviewing the context and importance of the research topic, further research questions have been raised; the following are addressed in the course of accomplishing the aims of this project:

- What is involved in the mechanism of migration-contamination?
- Which molecular markers can represent the most conclusive evidence available to support migration-contamination phenomenon in crude oil and how effectively can these be utilised?
- To what extent can it occur in deltaic basins so as to overprint the initial oil-source biomarker signatures?
- Are the occurrence and effects of migration-contamination quantifiable?
- What are the implications of misinterpretations based on occurrence of unusual biomarker distribution especially in Tertiary petroleum systems?

There is a need to re-examine established approaches to oil assessment based on common biomarkers, especially in many of the world's largest Tertiary deltas. For this reason, the proposed application of additional concentration-independent parameters, source definitive

parameters and/or indices of other biomarkers and other rare oil components such as unsaturated hydrocarbons (olefins) and non-hydrocarbon compounds in routine petroleum assessments is desirable.

It is expected that the outcome of this research will contribute to an increased understanding of the factors that control migration and its alteration mechanisms in reservoired hydrocarbons. Such knowledge should improve and increase accessible geochemical 'tools' for more effective application of molecular markers to hydrocarbon history assessments, particularly, in migration-contamination-prone Tertiary/deltaic systems. Ultimately, the answers to the above questions should enable testing of the study hypothesis, which is stated thus:

"The concentrations and distributions of hydrocarbon and non-hydrocarbon markers can be useful as indicators of migration-contamination in crude oil."

1.6.Aims and Objectives

As exploration for oil and gas, particularly in contemporary Tertiary deltaic environments, is currently being carried out, and with the growing economic significance now associated with progressively deeper offshore drilling, there is need to properly correlate deltaic oils to their true source rocks, and address any observed geochemical anomalies between Tertiary deltaic oils and their supposed source rocks.

The occurrences of olefins in produced crude oils and their distributions relative to other known biomarkers are used to determine possible incidences of migration-contamination, particularly in many vertically migrated Tertiary oils. In addition, the efficacy of carboxylic acids as markers of petroleum migration via immature or near-mature sequences, by comparison of their distributions in artificially-migrated oils from a laboratory migration study, is assessed. This approach is based on the premise that rare markers such as these, exhibit very low concentrations in non-biodegraded and mature oils and are therefore unlikely to be found in high concentrations in undegraded reservoired oils, whereas they occur in appreciable amounts in thermally immature sediments and some low-maturity oils (Meredith *et al.*, 2000).

The project uses a laboratory migration experiment in order to quantify the extent to which migrated oils can be 'contaminated' by organic components contained by carrier rocks. It is, therefore, the overall aim of this research to develop a geochemical approach for detecting

and understanding the occurrences and effects of migration alteration processes especially in Tertiary petroleum systems through characterisation and comparison of common and varying compositional factors in Tertiary deltaic oils represented by those of the Beaufort-Mackenzie-, Mahakam- (Kutei Basin) and Niger deltas as case studies. In order to achieve this, the following objectives were set:

- To obtain appropriate oil samples characteristic of worldwide Tertiary deltas;
- To isolate relevant organic compound fractions of case study oil field samples
- To analyse and characterise fractions at a molecular level, and use the concentrations and distribution of selected petroleum markers to detect possible migration-contamination in any of these oils;
- To carry out laboratory simulated migration experiments using immature organic rich rock and non-biodegraded mature oil;
- To determine the extent to which the initial compositions of migrated oils are 'contaminated'; and possibly identify any other solubilized organic components in the migrated oils;
- To determine the effect of oil migration on the distribution of acidic biomarkers in petroleum;
- To generate a dataset that could be useful for typifying Tertiary deltaic oils from various petroleum provinces.

1.7. Definitions of Keywords in the Study Context

This section defines some of the most frequently encountered keywords and analogous terminologies used in this work.

- **Petroleum** is defined as both crude oil and natural gas; ‘oil’ and 'gas' are descriptions applied to petroleum fluids under surface conditions of pressure and temperature (England et al., 1987); the terms petroleum, hydrocarbons, and oil and gas are synonyms.
- A **petroleum system** is defined here as a natural system that encompasses a pod of active source rock and all related oil and gas and which includes all the geologic elements and processes that are essential if a hydrocarbon accumulation is to exist (Magoon and Dow, 1994).
- **Migration** (of petroleum, oil or hydrocarbon), unless stated otherwise, is used here to refer to secondary migration of petroleum. This is the subsequent movement of petroleum within the reservoir rock, along faults or through permeable rocks, after it was first expelled (primary migration) from its source rock, over a considerable distance, to the trap or reservoir.
- **Migration-contamination** is used here to mean a mechanism of migration alteration whereby a migrating (or reservoired) petroleum fluid acts as a solvent for indigenous organic constituents of the sedimentary column along which it migrates, or the host strata; and as it is so called, the composition of such fluid is subsequently changed.
- **Olefins** are used here to encompass all known and identified unsaturated non-aromatic hydrocarbons. In this project they are isolated only from the aliphatic hydrocarbon fractions of the selected field and laboratory study samples. Also known as alkenes, these compounds contain only hydrogen and carbon with, at least, one double (not aromatic) or triple bond.
- **Carboxylic acids** are one of the non-hydrocarbon (NSO-containing) groups of organic components of geological samples. They are used here, synonymously with the terms organic acids, petroleum acids and acidic biomarkers.
- **Non-hydrocarbon compounds** include all resinous nitrogen-, sulphur-, and oxygen-containing (NSO) compounds representing the pentane-soluble fraction of crude oil. Asphaltenes also contain nitrogen, sulphur, and oxygen.
- **Migration markers**, -indicators, or -tracers are all used synonymously here to refer to any molecular marker, biomarker, specific parameter or component of geological

samples, to suggest or infer compositional changes in petroleum due to a migration alteration process.

- A **biomarker** (biological marker) is defined as a complex organic compound whose detection in the geological specimens signifies a distinct link with a known natural origin (Peters and Moldowan, 1993). These molecular fossils are ubiquitous in crude oils and petroleum source rocks in which their basic skeletons are maintained with minimal changes to their structures during oil formation processes.
- **Simulated migration** or artificial migration study is the laboratory component of this study involving experiments to simulate the sub-surface process of oil migration, using aliquots of oil and a porous media (rock), all of known composition, in order to measure compositional changes and/or redistribution due to migration-contamination.
- **Tertiary deltaic systems** consist of relatively young subsiding paralic sequences which build out seaward and commonly rank vertically and laterally in sedimentary succession from thick formation shale, clay-rich mud rocks to interlocking sandstone, siltstones and shales. Three well-known Tertiary systems are represented in this study.
- **Thermal maturity** of crude oil or source rock is used here as a measure of its state in relation to the maturity of its source at the time of expulsion, and as indicator of its hydrocarbon generation or potential respectively. The maturities of both oil and rock extracts are determined using geochemical techniques (biomarker parameters and ratios), and are used to broadly classify source rocks (or inferred source rocks of oil) as 'immature', sub-mature (early mature), mature, post-mature (late mature), and over-mature (lowest hydrocarbon potential).
- **Biodegradation** is an alteration process involving the sequential and systematic removal of various hydrocarbons resulting in modification of petroleum components (preserved or destroyed) usually within the reservoir. It slightest effects are evident in gas chromatograms of affected oils, in which low molecular weight *n*-alkanes are diminished prior to aromatic and other hydrocarbons.
- **Principal component analysis** (PCA) is a statistical analysis tool that uses an orthogonal transformation to convert a set of observations of correlated variables into a set of linearly uncorrelated variables called principal components. This transformation is defined in such a way that the first principal component has the largest possible variance, accounting for most variability in the data. These principal components are the eigenvectors (symmetric) of the covariance matrix.

Chapter 2 Background Literature Review

2.0. Introduction

The mechanisms of petroleum migration and accumulation, and their effects on crude oil composition remains one of the fundamental problems in petroleum geochemistry. A corresponding appreciation of this problem, and its consequences, is key to more accurate assessment of genetic relationships between various crude oils, especially those of similar location, and determining their source kitchens (Bonilla and Engel, 1986, 1988). This chapter, therefore, reviews relevant literature concerning the occurrence of a migration-induced phenomenon as well as the significance of the application of certain markers as indicators of its effects on the composition of petroleum.

2.1. Secondary Migration of Petroleum

Petroleum formation in fine grained source rocks, through organic matter (OM) deposition and preservation in the form of kerogen, and then hydrocarbon generation through thermal alteration of preserved OM, followed by expulsion (primary migration), migration (secondary) and accumulation of produced petroleum fluids in a trap, are well established (e.g. Tissot and Welte, 1984). Typically, secondary migration entails the buoyant movement of expelled oil and/or gas away from the generation site, up to >2 km and several hundred kilometres respectively, in both vertical and lateral directions through an inclined carrier bed and into porous, coarser-grained, more permeable reservoir rocks (England *et al.*, 1987, Peters and Moldowan, 1993, Larter *et al.*, 1996).

Primary migration is the petroleum expulsion from kerogen, and movement through its fine grained source rock to coarser grained carrier beds, while secondary migration is the movement of petroleum through coarser grained and permeable carrier beds to a reservoir or trap (Tissot and Welte, 1984, Hunt, 1995). The former type of migration is not relevant to this study, owing to the fact that the migration-contamination phenomenon is a mechanism involving the solubilisation of organic components within the migration conduit (e.g. Bonilla and Engel, 1988, Curiale and Bromley, 1996b, Curiale, 2002), and hence is rarely referred to in this work.

In a bid to better understand this most critical process (migration) in petroleum accumulation, improved methods and type of exploratory data acquired during the search for new petroleum resources is required. This could be achieved by obtaining information about the distance travelled, route taken and the possible alterations undergone by oil during

its migration from source to the reservoir (England *et al.*, 1987). These factors are the outcomes of complex migration processes leading up to accumulation, and cannot be directly measured by seismic or other geophysical surveys. Hence petroleum geochemists have, for several decades, sought to quantify these processes by geochemical analysis of reservoired oil using changes in the amounts and distributions of a variety of compounds as migration indicators (Larter *et al.*, 1996).

Migration of petroleum into and through a geological column may result in detectable changes in the produced oil, condensate and gas (Curiale and Bromley, 1996a). These alterations, as they affect the source-derived biomarker signature of oil, have been reported to be the consequences of a number of processes occurring from oil generation and expulsion from source rocks, to secondary migration and accumulation. During its initial stages in migration (including primary migration), mobile petroleum is more dispersed and exposed to contact with mineral surfaces and resultant sorption effects (Krooss *et al.*, 1991). However, these processes have been classified by Curiale and Bromley (1996a) and Hughes and Dzou (1995) as mainly occurring during secondary migration and after accumulation.

2.2. Occurrences and Evidence of Migration-Contamination

The past few decades have witnessed observations of the modification of a crude oil molecular make-up due to differential loss (Hoffman *et al.*, 1984), redistribution or fractionation (Brothers *et al.*, 1991, Dzou and Hughes, 1993, Curiale and Bromley, 1996a) of oil components during secondary migration. However, the reverse process involving ‘addition’ of typical components to oil after expulsion from its source rock, though lacking detailed documentation, is not uncommon. This phenomenon has earlier been acknowledged in various Tertiary deltaic systems and is generally referred to as migration-contamination (Curiale, 2002). A modified graphical illustration, with respect to study objectives, is shown in Figure 2.1.

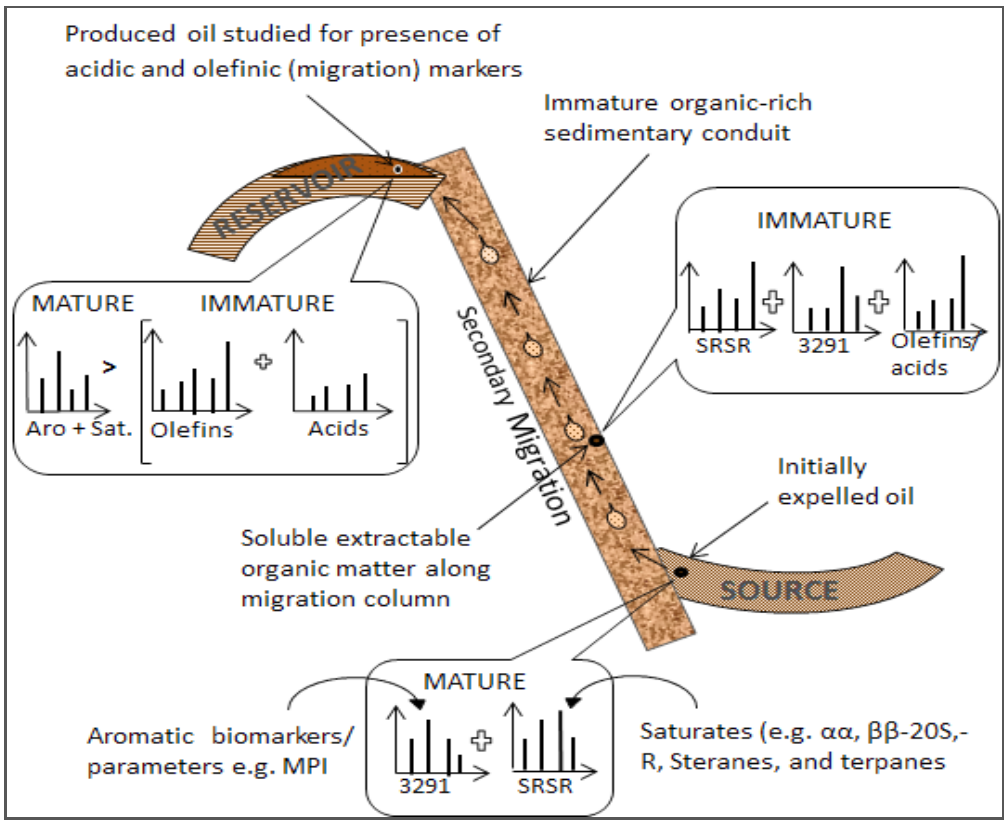


Figure 2.1 Cartoon showing the path of an oil migration and changes in oil composition attributed to migration effects. Oil can travel from source to reservoir along a column of immature, organic-rich sediments (modified from Curiale, 2002).

Migration-contamination is defined as a process whereby crude oil, either en route or trapped, acts as a solvent for indigenous organic compounds in the host stratigraphic column (believed to be unrelated to the migrating crude) or reservoir section, which are usually organic-rich and thermally immature (Curiale and Bromley, 1996a, Curiale and Frolov, 1998). Hence, the findings of several studies (e.g. Table 2.1) on this process, in various settings using diverse approaches and methods, have established that the solubilised organic contents are generally lower in maturity than those comprising the crude oil.

Quantifiable evidence of migration-contamination has been shown to consist of 'mixed' thermal maturity signals or unusual distributions of biomarkers in 'exposed' petroleum (Peters and Fowler, 2002). These indications are given in some documented examples (Table 2.1) of this occurrence in crude oils well-known petroleum provinces of the world (e.g. Rullkötter *et al.*, 1984, Philp and Gilbert, 1986, Ekweozor and Udo, 1988, Riva *et al.*, 1988, Jaffé *et al.*, 1988a, Bac *et al.*, 1990, Thompson and Kennicutt II, 1990, Ukpabio *et al.*, 1994, Hughes and Dzou, 1995, Curiale and Frolov, 1998, Curiale *et al.*, 2000, Curiale, 2002, Li *et al.*, 2008). The U.S. Gulf (of Mexico) Coast has oils with some of the best examples of migration-contamination. Intensive studies have been carried out on its various locations (Thompson and Kennicutt II, 1990, Comet *et al.*, 1991, Curiale and Bromley, 1996a).

Table 2.1 Instances of published migration-contamination reports; this table contains only those instances with existing evidence to support the claim as compiled by Curiale (2002) and adapted for this review.

Province	Basin/Country	Main findings	References
Australia	Gippsland Basin	Computerised GC/MS revealed presence of thermally unstable ββ isomers of hopane-type triterpanes, and C-22 diastereoisomers(*S*/*R*), in unusual proportion (1:9), probably due to migration through interbedded coal, containing unusual hopane distribution.	Philp & Gilbert, 1982; 1986.
Asia	Mahakam Delta, Indonesia	Varying 22*S* & 22*R* of the ββ–C_{30} hopanoic acid in various coals and crude oils. Variations with increasing migration distance include increasing long chain acids (LCA) with OEP<1, and cyclic acids; indicative of solubilisation of immature OM.	Jaffe et al., 1988a & b; Hoffman *et al.*, 1984.
	Offshore Brunei	Examination of a series of offshore oils and onshore rocks revealed variations in mixed organic input in the sample set, an indication of extensive migration-contamination, with respect to the tetracyclic and pentacyclic hydrocarbons.	Curiale *et al.*, 2000.
	Surma Basin, Bangladesh	Many of the gas accumulations are associated with retrograde condensates whose compositions are defined by two distinct source facies and by the solution/exsolution effects of vertical migration of oil.	Curiale *et al.*, 2002.
	Turpan Basin, China	Large differences in the absolute concentrations of biomarkers in rock extracts of various source intervals and 'coaly' oils most likely resulted from mixing and solubilisation during migration through fractured coal seams along deep-seated faults.	Li *et al.*, 2001.
Africa	Niger Delta, Nigeria	Presence of triterpenes including oleanenes, baur-7-ene, and urs-12-ene in a Niger Delta oil; attributed to contamination within the thermally immature Agbada shales, en-route and in-reservoir. The oil maturity signature appeared to be unaltered by this occurrence.	Ukpabio *et al.*, 1994.
	Angola	Sterane maturity pattern showed Angolan oils as condensates, but with abundant C_{27}αα20*R* indicating immaturity.	Peters & Moldowan, 1993.
	Gulf of Suez, Egypt	Observed significant differences within oils in respect of abundant gammacerane, and oleanane indices (>20%), indicating possible mixing or solubilisation of indigenous OM from adjacent sediments.	Rohrback, 1983.
North America & Caribbean	Simpson-Umiat Fields, Northern Alaska	Absolute concentrations of biological markers (steroids and triterpenoids) in crude oils revealed oil mixing at different maturities levels and uptake of biomarkers from reservoir rocks matrix (in-reservoir alteration).	Rullkötter *et al.*, 1984.
	Cook Inlet Basin, southern Alaska	Proposed that a high (41") API oil of Cook Inlet Basin is a mixture of Jurassic-derived oil with low (5%) Tertiary input derived from coals interbedded with the reservoir sands. Reservoir overprinting is believed to have altered the oil biomarker signature.	Hughes and Dzou, 1995.
	San Joaquin Basin, California	Correlation of the Moreno Formation to 3 reservoired oils in the San Carlos sandstone, reflected biomarker contributions from the former, by the occurrence of both alkanes (28,30-bisnorhopane) and alkenes (dammarenes and diasterenes), at variable maturities.	Bac *et al.*, 1990.
	Vermilion 14 Field, Offshore Louisiana	Migration-contamination is supported by the occurrence in the oils of unsaturated and thermally unstable hydrocarbons, including oleanenes, dammarenes, and diasterenes, as well as molecular maturity ratios indicative of immature OM.	Curiale & Bromley, 1996a; Curiale & Frolov, 1998.
	Offshore Gulf of Mexico, USA	Characterised by molecular maturity imbalances such as the presence of unsaturated hydrocarbons known to be unstable at petroleum generation temperatures for these oils.	Thompson & Kennicutt, 1990; Comet *et al.*, 1991.
	Azua Basin, Dominican Republic	Recognition of molecular and isotopic imbalances in the Mesozoic oils and condensates of the Azua Basin due to presence of abundant C_{30}-C_{35} $\Delta^{17,21}$ hopenes.	Walters *et al.*, 1995.

In spite of the several acknowledged published examples of migration-contamination, the extent of this phenomenon in oils and its implications and frequency of occurrence are perceived quite individually by many authors. In some other instances, the effects of this

process have not been considered at all in the interpretation of geochemical data, or may have been invoked (perhaps, wrongly) to justify a peculiar biomarker distribution especially where no other supporting data has been employed (Curiale, 2002).

2.2.1. *Geological Conditions for Migration-Contamination*

Most documented evidences of migration-contamination support the proposition that certain characteristic requirements must be met by a petroleum and the sedimentary sequence in place for this process to be viable and effective. In other words, its occurrence is limited by certain geochemical and geological conditions (Curiale and Frolov, 1998, Curiale, 2002). It is, therefore, necessary that assessments of composition alterations attributable to secondary migration processes be conducted on appropriate geochemical systems where the oil(s) have been generated by a source rock with well-defined biomarker and geochemical features, and have travelled along constrained migration paths and/or accumulated in immature sections (Trindade and Brassell, 1992). Such conditions are only wholly or partially attainable in Tertiary and/or younger Deltaic petroleum systems and, in some rare instances, pre-Tertiary and post-Tertiary systems (Curiale and Frolov, 1998).

A typical depositional setting in a Tertiary deltaic petroleum system for the occurrence of migration-contamination includes thick, rapidly deposited sedimentary sections cut by major faults, essentially the listric type. The presence of listric faults is the primary cause of the extensive vertical migration of petroleum into overlying, biomarker-rich carrier beds (Curiale, 2002). An example of such setting, as in the Niger Delta, is represented in Figure 2.2. Here, the oil-bearing, shallower rocks must be organic-rich, thermally immature and contain potential reservoir and structural traps (Hughes and Dzou, 1995, Curiale and Bromley, 1996a). This type of setting characterises the petroleum systems of many Tertiary deltaic basins and creates the potential for oil to extract organic matter as it migrates along its path to a trap (Curiale, 2006).

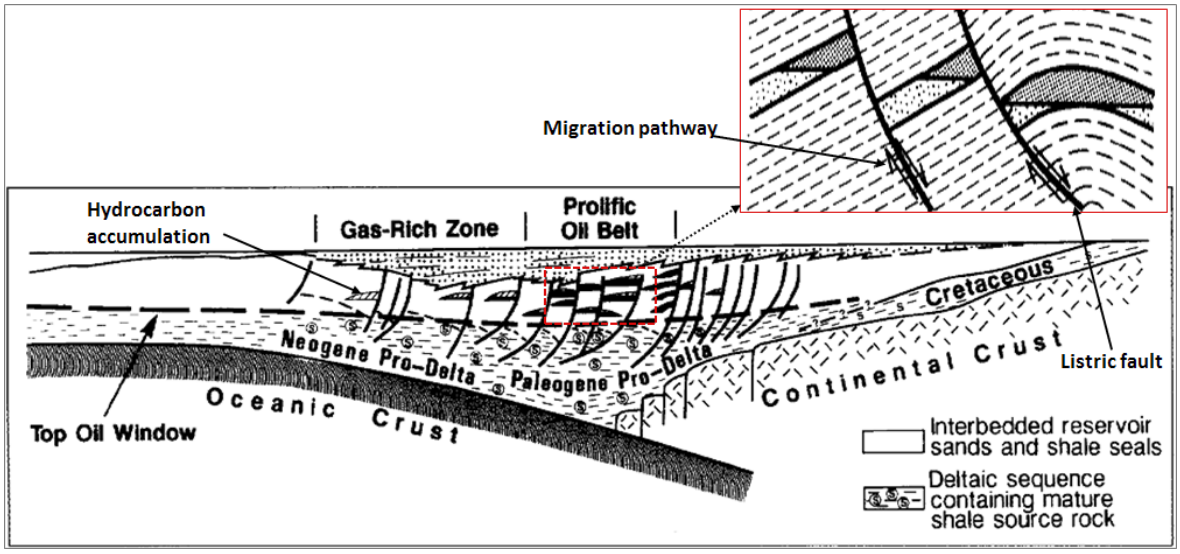


Figure 2.2 Schematic representation of a normally charged and vertically drained petroleum system, modelled after the Niger Delta, Nigeria. Tertiary deltaic sediments are usually vertically drained, mainly due to the presence of listric faults (modified from Magoon and Dow, 1994).

2.3. Crude Oil Composition Alteration Processes

It is a well-known fact that the biomarker profile of an oil, which should have been an imprint of its source, may be altered by a number of processes occurring post-generation and expulsion. These processes have been categorised by Hughes and Dzou (1995) into en route (along migration path) and in-reservoir alteration processes, although some (like water washing) can occur both during migration and in-reservoir. A considerable amount of literature has been published on migration alteration processes which include, but not limited to, geo-chromatography (Jaffé *et al.*, 1988b, Brothers *et al.*, 1991, Krooss *et al.*, 1991), migration fractionation (Thompson and Kennicutt II, 1990, Dzou and Hughes, 1993, Curiale and Bromley, 1996a) and leaching or solubilisation of organic components from sediments along migration columns, referred to, here, as 'migration-contamination' (Peters and Moldowan, 1993, Curiale and Bromley, 1996b, Curiale and Frolov, 1998, Curiale, 2002). On the other hand, in-reservoir alteration processes have been studied much more over the past 30 years and these include biodegradation (Jaffé and Gallardo, 1993, Nascimento *et al.*, 1999, Meredith *et al.*, 2000, Watson *et al.*, 2002), water washing (Trindade and Brassell, 1992, Barth and Bjorlykke, 1993), thermal intrusion/cracking (Tissot and Welte, 1984), radiolysis (Frolov and Smirnov, 1994, Melikhov *et al.*, 1996, Curiale and Frolov, 1998) and reservoir overprinting (Hughes and Dzou, 1995). The effects of reservoir overprinting has been likened to those due to migration-contamination because the mechanism leading up to the former also involves the uptake of soluble biomarkers, not en route, but from interbedded organic-rich reservoir shales (Philp and Gilbert, 1982, Rullkötter *et al.*, 1984, Peters and Moldowan, 1993). Water washing could occur during migration of oil through water-

saturated carrier beds, as well as in the reservoir, where it is usually associated with biodegradation.

In addition, the effects of source-related changes on petroleum have been recognised (Tissot and Welte, 1984, Hughes and Dzou, 1995). Such factors affect the composition of expelled petroleum and include the organic matter input, depositional environment, burial depths and thermal maturity of the source rock. The principal depositional conditions can be characterised by the abundance of markers of organisms specific to a particular environment (e.g. Brassell *et al.*, 1986). The bulk composition of expelled crude oil is controlled by the maturity of the source rock, while the extent of maturation also determines the structural configurations of the oil components (Trindade and Brassell, 1992). The recognition and interpretation of these processes are, however, convoluted by limiting factors such as mixing of petroleum (Brooks, 1986a). Nonetheless, it is very important to better appreciate the factors controlling their individual occurrence and scale in order to effectively apply them to petroleum studies.

2.3.1. *Secondary Migration Influences*

Secondary migration-induced compositional alterations, with their proposed incidence, have remained a subject of controversy amongst many researchers. In as much as the factors that control migration in any given geologic environment are unique and complex (Bonilla and Engel, 1986), some dynamics that could produce changes to the bulk composition of petroleum during migration (Trindade and Brassell, 1992) have been proposed by many authors to occur through different migration mechanisms (e.g. Lafargue and Barker, 1988, Krooss *et al.*, 1991, Larter and Mills, 1991, Curiale, 2002). However, the description of oil migration phenomenon based on just one of these mechanisms would be far too simplistic (Bonilla and Engel, 1986) given their complex manifestations. These factors are briefly discussed in the following sections.

Geochromatography

Geochromatography has remained a controversial process perceived and accounted for differently by many authors (e.g. Seifert and Moldowan, 1981 etc., Carlson and Chamberlain, 1986, Jaffé *et al.*, 1988b, Brothers *et al.*, 1991, Krooss *et al.*, 1991). This phenomenon has been hypothesized to occur in geological systems comprising of two or

more immiscible components which include, at least, one stationary phase (the mineral matrix in a stratigraphic carrier bed) and a mobile phase consisting of biomarkers and other compounds (Krooss *et al.*, 1991, Peters and Moldowan, 1993). While this process might be favoured in geological settings with special elements such as clay-rich sandstone in an oil-wet system (Carlson and Chamberlain, 1986, Brothers *et al.*, 1991), its effects on organic compounds are thought to be more noticeable in laboratory simulation studies (e.g. Brothers *et al.*, 1991), but are subject to significant limitations on a field scale (e.g. Leythaeuser *et al.*, 1984, Trindade and Brassell, 1992). In terms of the mobile oil components, properties such as polarity, molecular weight and chirality influence their behaviours on exposure to various adsorptive materials (Peters and Moldowan, 1993). Brothers *et al.* (1991), in their experiments with synthetic oils, demonstrated that simple nitrogen compounds are more susceptible to geochromatographic interactions and that *n*-alkanes are enriched relative to the aromatic hydrocarbons and sulphur compounds in the least retarded fraction. Changes in the relative proportions of the αββ- and ααα-sterane isomers and the enrichment of the tricyclic terpenoids over their pentacyclic counterparts have also been reported (Seifert *et al.*, 1979, Seifert and Moldowan, 1981). It is without doubt that geochromatography may alter the distribution of biomarkers in oils but the addition of extraneous organic components (migration-contamination) to migrating oil could also considerably affect the distribution of certain components.

Migration Fractionation or Phase-controlled Partitioning

The process of migration fractionation and its effects on petroleum composition has been widely recognised (Thompson, 1987, Thompson, 1988, Zhusheng *et al.*, 1988, England and Mackenzie, 1989, Larter and Mills, 1991, Dzou and Hughes, 1993, Curiale and Bromley, 1996b, Curiale *et al.*, 2000, van Graas *et al.*, 2000, Eseme *et al.*, 2007). Also referred to as evaporative-, differential migrations and phase-partitioning by some authors (e.g. Thompson, 1987, Dzou and Hughes, 1993, van Graas *et al.*, 2000), the term 'migration fractionation' is a secondary alteration process suggested to describe a number of phenomena in which a gas-condensate cap separates from its associated migrating or reservoired oil in the subsurface (Thompson, 1988, England and Mackenzie, 1989, van Graas *et al.*, 2000). This is the result of a pressure-drop (<bubble point) due to long-distance vertical/semi-lateral migration of a petroleum (single-phase fluid) from deeply buried source rock to shallower, in-reservoir accumulations, a fault or fracture, and/or addition of relatively

dry gas to an oil reservoir from depth (England *et al.*, 1987, van Graas *et al.*, 2000, Curiale, 2008).

These partitioning effects have been recorded in many oil basins of the world but limited to gas condensate-rich systems due to the influence of phase behaviour or gas-oil ratios (GOR) of expelled petroleum (England and Mackenzie, 1989). Evidence of fractionation was first reported in oils of the Mahakam Delta by Silverman (1965) who distinguished it from the secondary migration phenomenon by the term 'separation-migration'. Recorded effects may include large variations in the bulk properties of petroleum such as the API gravity, GOR, and certain molecular and carbon isotope indicators (Dzou and Hughes, 1993, Curiale, 2008) which are commonly assessed in crude oils. More importantly, the residual oil exhibits the following typical changes in their hydrocarbon profile: loss of light hydrocarbons ($<C_9$), increased aromaticity, and *n*-alkanes + naphthenes relative to branched isomers and decreased parafinicity (Trindade and Brassell, 1992).

An understanding of this process could be useful for interpretation of the origins of petroleums whose original composition may have been altered by this process especially in gas-condensate prone migration systems. In addition, the depth at which the single-phase fluids begins to separate can be estimated and used to determine single- or two-phased accumulations (Noble *et al.*, 1991). It is, however, important to consider the effects of migration-induced processes when interpreting geochemical data for residual oils and gas-condensates so as to make reliable assessment between the oil, gas condensate and their source rocks (van Graas *et al.*, 2000).

Losses in Solution (Water washing)

Petroleum migrates primarily through water-wet systems where relatively soluble gasoline range hydrocarbons can be lost in solution by the process of water washing (Lafargue and Barker, 1988). Water washing implies the removal of these water soluble components from crude oil and can also occur in the reservoir or as a result of distant lateral migration in water-saturated porous beds (McAuliffe, 1979, Lafargue and Barker, 1988). It usually occurs alongside petroleum biodegradation which typically subdues the effects of the former (Trindade and Brassell, 1992).

Normal alkanes, cycloalkanes and aromatic hydrocarbons are prone to aqueous solubilisation with the aromatics being more soluble than their *n*-alkane counterparts. This

solubility decreases with increasing carbon number (McAuliffe, 1979). Nonetheless, the retention or removal of compounds during water washing studies does not exactly correspond to their relative solubilities (Lafargue and Barker, 1988). Features indicative of this process have been proposed by Lafargue and Barker (1988) to include preferential removal of aromatics, depletion of sulphur compounds in the $<C_{15}$ fraction and loss of dibenzothiophenes (DBTs). A similar effect on the redistribution of such polar materials as carboxylic acids in geological samples during migration of petroleum through immature shales and coals has been proposed and studied in detail (Jaffé *et al.*, 1988a, 1988b). With no systematic trend observed in their study of altered oils with migration distance, the findings of Trindade and Brassell (1992) seem to agree with the proposal of Lafargue and Barker (1988) that water washing is dominant and more effective in the reservoir, and that its effects are minimal during migration.

2.3.2. *In-Reservoir Alteration*

Biodegradation

Biodegradation of crude oil is an important alteration process, especially in subsurface oil reservoirs which can occur in the presence of hydrocarbon-degrading aerobic, anaerobic or methanogenic microbes, as well as other conditions necessary to nourish and support microbial life (Connan, 1984, Watson *et al.*, 2002, Aitken *et al.*, 2004). Its profound effects on the hydrocarbon composition of crude oil have also been widely reported and reviewed (e.g. Connan, 1984, Volkman *et al.*, 1984, Watson *et al.*, 2002). The process entails sequential and systematic removal of various hydrocarbons resulting in modification of in-reservoir petroleum components (preserved or destroyed); selective degradation of specific isomers within individual compounds classes and most probably the production of acidic compounds as observed in many shallow oil reservoirs (Head *et al.*, 2003). Many geochemical studies have concluded that some oils undergo biodegradation in the reservoir (e.g. Connan, 1984, Curiale, 1991, Taylor *et al.*, 2001, Head *et al.*, 2003). This is evident from the changes in the relative *n*-paraffin concentrations because *n*-alkanes are removed prior to aromatic hydrocarbons. Many components of petroleum are believed to be altered in concentration and distribution due to the biodegradation process and these include well-documented polar (NSO) compounds such as carboxylic acids, carbazole and its derivatives, and phenol and its derivatives (Jaffé and Gallardo, 1993, Taylor *et al.*, 2001, Lucach *et al.*, 2002). Carboxylic acids are an important class of non-hydrocarbons in biodegraded oils

because they are a major determinant of oil acidity in form of Total Acid Number (TAN) parameter, with its economic implications (Meredith *et al.*, 2000, Watson *et al.*, 2002) due lower oil selling price, cost of bioremediation in the event of oil spill, and most significantly the cost of tackling associated pipeline corrosion and refinery problems. They have also found application as indicators of migration in crude oils owing to their unusual abundance in certain mature, non-biodegraded oils (e.g. Jaffé *et al.*, 1988a, Jaffé *et al.*, 1988b, Jaffé and Gallardo, 1993, Galimberti *et al.*, 2000). The extent to which this process alters the composition of the oil has been classified as ranging from 'no' biodegradation to 'light' through 'medium' to 'heavy' biodegradation using a number scale of 1 to 10 (light to severe) (Fig. 3.62 in Peters and Moldowan, 1993, Wenger and Isaksen, 2002, Head *et al.*, 2003).

Thermal Alteration

Episodic intrusion of molten rock can expose the components of petroleum to high temperatures which may result in the formation of new and additional related components usually by the mechanism of thermal cracking (e.g. Bazhenova *et al.*, 1998). A similar process involving the extraction of hydrocarbons from oil-source formation by heated waters have also been reported; this type of compositional alterations occur in unique hydrothermal systems where both deep-seated magmatic temperatures and thermal waters of wide-ranging temperatures (40-400^{o}C) co-function towards the alteration process, which is thought to be viable under high water/rock volume ratio conditions (Simoneit, 1984, Bazhenova *et al.*, 1998). Instances of these systems revealed their crude oils to be of immature and dominantly marine source, and contain considerable amounts of olefins. These hydrocarbons have been shown to be of hydrothermal, rather than radiogenic origin (Bazhenova *et al.*, 1998). Examples of well-known hydrothermal systems include the volcano Uzon caldera, eastern Kamchatka Basin and Guaymas Basin, Central Gulf of California (Simoneit, 1984, Simoneit *et al.*, 2009). While oil migration may see an enrichment in crude oil of paraffins and depletion of the asphaltenes, resins and the polar (NSO) compounds, these changes may appear to be similar to those reported in thermal alteration events by Silverman (1965), Tissot and Welte (1984) and, most recently, Simoneit *et al.* (2009).

2.4. Applications of Molecular Markers to Petroleum Studies

2.4.1. *Maturity Assessment and Evaluation*

The thermal maturity of a source rock or a set of oils can be evaluated using a number of molecular maturity ratios and parameters. Isomer ratios of triterpenoids are often applied as parameters for the assessment of thermal maturity (e.g. Brooks, 1986a, Ekweozor and Telnaes, 1990, Curiale, 1991, Peters *et al.*, 2005). Over the past several decades, a huge number of studies on petroleum samples from many well-known oil provinces have shown the utility of various molecular marker parameters for this purpose. Some of these commonly applied maturity markers include aromatic hydrocarbons, including aromatic steroid hydrocarbons, normal and isoprenoid alkanes, diasteranes, regular steranes, and triterpanes (Peters et al., 2005). Many biomarker parameters such as the C_{29} sterane isomer ratios, sterane/hopane ratio and other marker combinations have been used as maturity tools and in correlation studies. However, caution should be applied when using biomarkers to assess maturity as their concentration may well be controlled by other established geological processes such as migration, biodegradation, organic matter source etc. (Peters and Moldowan, 1993). Other characterisation tools such as the abundance and distribution of rare components of petroleum (e.g. olefins, carbazoles and fatty acids) are now available to evaluate the indigenousness of oils or rock extracts and should be used alongside the routine biomarkers (e.g. Jaffé *et al.*, 1988b, Clegg *et al.*, 1997, Curiale and Frolov, 1998).

2.4.2. *Genetic and Geological Age Relationship*

Genetic correlations of oils requires the use of a variety of specific biomarkers, and are based on the premise that the compositional attributes of a source rock are inherited by the oil it expelled (Peters and Moldowan, 1993). For example, triterpane distributions in sediments and crude oils are commonly used for oil-oil and oil-source rock correlations in petroleum studies (Hoffman *et al.*, 1984, Rullkötter *et al.*, 1994, Peters *et al.*, 2005). The unusual nature and occurrence of certain terrigenous compounds such as 18α(H)-oleanane and isomeric C_{28} triterpanes of the lupane series are excellent markers of oil-oil correlation studies (Brooks, 1986a). For instance, the absence of oleananes in the majority of marine oils such as the North Sea oils is very consistent with the Jurassic age of these oils, while its presence is typically an indication that the oils containing it comprise a significant proportion of terrigenous sourced material, and are generated from source rocks of Late Cretaceous age or

younger (Peters and Moldowan, 1993; and the references therein). However, a positive correlation does not always necessarily prove a relationship between samples, but a negative correlation completely rules out any of such relationships. In order to determine the geological history of a petroleum, an understanding of the age-based distribution of its biomarker make-up is necessary. This knowledge greatly facilitates oil-source rock correlation assessments. With the evolution of new organisms (e.g. angiosperms), changes in biota (e.g. during the Cretaceous/Tertiary), and major geologic events (e.g. oceanic anoxia), there are many candidates for biomarkers that can distinctly be linked to geological age (Peters and Moldowan, 1993).

2.4.3. *Source Characteristics and Depositional Environment*

Over the past several decades, many molecular markers have been applied to indicate the source organic matter, and its depositional environment, from which an oil and its source rock were derived (Peters and Moldowan, 1993). Biological marker distributions enable the characterization and distinguishing of ancient marine and non-marine petroleum source rocks (e.g. Mello and Maxwell, 1990). They also provide indicative conditions for the distinguishing or correlation of oils derived from source rocks deposited in different environments such as marine, lacustrine, saline/hypersaline and terrestrial (Brassell *et al.*, 1986, Philp and Gilbert, 1986, Talukdar *et al.*, 1986, Hwang *et al.*, 2002). The application of specific markers such as certain linear and isoprenoid alkanes, steranes and terpenoid hydrocarbons to imply or suggest a source (or common source) kitchen for oils is widespread. It is a general fact that the compositional make-up of an oil or source rock is a reflection of the precursor compounds in the organisms from which the organic matter was derived during deposition, and thereby can provide information about the major conditions of the environment (e.g. Brassell *et al.*, 1986).

2.4.4. *Biodegradation Studies*

The use of biomarkers have been routinely applied to the study of biodegradation of petroleum components during migration and accumulation (e.g. Seifert and Moldowan, 1979, Volkman *et al.*, 1984, Peters and Moldowan, 1991, Jaffé and Gallardo, 1993, Meredith *et al.*, 2000, Taylor *et al.*, 2001, Watson *et al.*, 2002). For instance, variations in simple *n*-paraffin parameters across sample sets have been studied and applied as indicators of biodegradation. In a study of several reservoired Paleogene oils from the Canadian Beaufort

region, Curiale (1991) concluded that these oils are biodegraded based on molecular data derived from whole oil gas chromatogram fingerprint. Here, decreasing pristane/phytane, increasing pristane/*n*-C_{17} alkane ratios, and decreasing short chain *n*-alkanes correspond to increasing biodegradation. On the other hand, an increase in the amount of non-hopanoid pentacyclic triterpanes, (e.g. oleanoids and lupanoids), relative to hopane also shows positive indication to increasing biodegradation, probably due to the selective removal of the 17α(H) hopane series by degrading microbes (Rullkötter and Wendisch, 1982). In general, the sequence of increasing resistance of biomarkers to biodegradation is: light paraffins < isoprenoids < steranes < hopanes/diasteranes < aromatic steroids < porphyrins (Peters and Moldowan, 1991). However, Peters and Moldowan (1993) used a 'quasi-stepwise' order to tentatively indicate that some components of more biodegradable compound class may be resistant to biodegradation even after commencement of the process on the next more resistant ones. Biodegradation can alter commonly used maturity and correlation parameters; hence, it is important to recognise the level of biodegradation attained by every sample under evaluation when using molecular parameters to evaluate this process (Curiale, 1991).

2.5. Some Common Markers in Tertiary Deltaic Oils

Many reports have documented the biomarker profile of petroleum in the early stages of generation as well as the changes in these profiles with further increasing generation, expulsion and migration (e.g. Cornford *et al.*, 1983, Jaffé and Gardinali, 1990, Forbes *et al.*, 1991, Li *et al.*, 2001). A newly generated crude oil is known to contain relatively high amounts of biomarkers (e.g. terpanes, steranes) compared with the normal and isoprenoid alkanes. Further diagenesis (and catagenesis) with increasing oil generation may be followed by thermal degradation and subsequent dilution of the originally existing components. This is demonstrated by a situation where a mature oil comes in contact with the surface of immature, biomarker-rich sediment, resulting in a noticeable change to the biomarker distribution in the oil (cf. Curiale, 1995, Hughes and Dzou, 1995).

Tertiary deltaic oils are known to contain relatively high amounts of certain steranes and triterpanes (e.g. $\geq C_{26}$ *n*-alkanes, pristane, C_{29}-steranes, oleanane, lupane etc.) suggesting a terrestrial, higher plant contribution to the oils (Peters and Moldowan, 1993). Many of the components (and isomers) of these common groups of biomarkers have been identified in the subject oils from around the world (Woodhouse *et al.*, 1992). Although these major biomarker groups are not discussed in full detail in the following sections, their widespread occurrence, characteristics and functions in these oils are summarized.

2.5.1. *Normal and Isoprenoids Alkanes*

A distinguishing attribute of many non-biodegraded Tertiary oils is the presence of an extended ($\geq C_{32}$) mixture of normal alkanes (Volkman *et al.*, 1984), cycloalkanes and long-chain ($\leq C_{40}$) isoprenoids. The *n*-alkane distribution in Tertiary oils is mostly that of a normal (unimodal) pattern, with some degree of skewness. It is dominated by *n*-alkanes in the range of nC_{14} – nC_{28}, peaks at nC_{16} or $nC_{17,}$ and shows a slight predominance of even/odd preference *n*-alkanes around C_{18}-C_{26} (Sonibare *et al.*, 2008). Philp and Gilbert (1986), in an extensive characterisation of various Australian oils, proposed a head-to-tail orientation for identified isoprenoid alkanes suggesting their origin from well-known polyprenols occurring in plant conifers. A high paraffin and wax content (abundant C_{24}-C_{32} *n*-alkanes), together with high pristane/phytane ratios (~3-10) are indicators for oils derived from source rock with a significant terrigenous organic material contribution, and deposited in a predominantly oxic swamp paleoenvironment (Ekweozor *et al.*, 1979a, Hoffman *et al.*, 1984).

2.5.2. *Steranes and Diasteranes*

Another common characteristic of oils which contain a high concentration of terrigenous organic matter is the relatively low concentration of steranes compared to the triterpanes (e.g. Hoffman *et al.*, 1984, Philp and Gilbert, 1986). Derived from peak intensities in the m/z 191 to 217 mass chromatograms, respectively, terpane/sterane ratios of at least greater than 1 and up to 10 or more in such oils are not unusual. Their distribution in most of these oils is more defined than those of the terpanes. The prevalence of the C_{29} steranes and diasteranes, lower abundance of C_{28}-, and very low amounts of C_{27}-steranes are clear indicators of terrigenous organic matter input to the source of these oils where such alteration factor as biodegradation has been ruled out (Czochanska *et al.*, 1988, Peters and Moldowan, 1993).

On the other hand, biomarker parameters, such as those associated with increasing abundance of diasteranes relative to steranes, would suggest that the oils may have been generated from source rocks containing abundant clay minerals since their occurrence are generally attributed to clay-catalysed rearrangements of sterol and sterene precursors during diagenesis (Rubenstein *et al.*, 1975). Compared to the regular steranes, diasteranes have been found to be more thermally stable (Peters and Moldowan, 1993), and this would account for their increasing relative concentrations with increasing maturity.

Steranes can be indicators of common source material for differently accumulated oils due to similarities in their distributions in such oils; but only when they are not biodegraded or 'contaminated' during migration and accumulation. The indicative ratios based on C_{29} 20*R*/20*S* isomers can show inconsistent values in biodegraded samples because the biodegradation process favours the preferential depletion of the 20*R* epimer (Seifert and Moldowan, 1979) while 'migration-contaminated' oil would most likely be enriched in 20*R*-C_{29} steranes, leaving the diasteranes unaltered (Philp and Gilbert, 1982, Philp, 1994).

2.5.3. *Triterpanes*

Pentacyclic triterpanes are widespread components of geological samples (Brooks, 1986a). They are, however, more abundant in petroleum than in sediments, and include the hopanes (and moretanes), oleananes (or ursane) and the lupane series (Ekweozor *et al.*, 1979a, Nytoft *et al.*, 2002, Peters *et al.*, 2005). Hopanes and oleananes are the most significant pentacyclic triterpanes in many recognised Tertiary oils (Ekweozor *et al.*, 1979a), but their respective distributions in these oils differ significantly from oil to oil.

Although first discovered in Niger Delta oils by Whitehead (1973) more than four decades ago, the geochemical applicability of oleananes only became significant more than a decade after their origin was first postulated. This was subsequent to their detection and identification in geological samples from other petroleum provinces of the world, as well as in (pre-Tertiary) late Cretaceous rocks (Ekweozor and Udo, 1988, Riva *et al.*, 1988). Oleananes are classed as non-hopanoid pentacyclic terpanes (Curiale, 1991) and have been used synonymously with the term terrigenous triterpanes (Rullkötter *et al.*, 1994). Their high concentrations in certain oils have been attributed to a large terrestrial, land plant source input. Their absence, however, does not exactly dismiss a terrestrial origin for oils (e.g. oils of Gippsland Basin, Philp and Gilbert, 1986, Woodhouse *et al.*, 1992). They are believed to be hydrogenation products of oleanenes during diagenetic or catagenic processes as demonstrated by ten Haven and Rullkötter (1988) and Rullkötter *et al.* (1994) in their oleanene isomerisation studies. Both studies indicated that hydrogenation occurs mainly through olean-18-ene and less predominantly through olean-12-ene and 18α-olean-12-ene. These findings contrasted with those of Ekweozor and Telnaes (1990) which suggested that the main hydrogenated oleanene isomer is olean-13(18)-ene. Increasing 18α- and decreasing 18β-oleanane relative to total oleanane content, with higher maturity has been shown to be an effect of the higher thermal stability of the 18α-isomer (e.g. Rullkötter *et al.*, 1994)

contrary to earlier proposed temperature-dependent conversion of oleanene to 18α-oleanane (e.g. Ekweozor and Telnaes, 1990).

Also classed as non-hopanoid pentacyclic triterpanes, the lupane series has been shown to have a strong relationship with oleananes. Their abundance vary proportionally with those of 18α (H)-oleanane in relative to 17α (H)-hopane (oleanane index), and this has led to the conclusion that lupanes are higher plant, angiosperm-derived components, and that their presence can also be used to support a Tertiary/L.Cretaceous source for oils (e.g. Curiale, 1991, Nytoft *et al.*, 2002). This proportionality strongly supports higher plant (angiosperm) precursors for lupanes and other related components often seen in their m/z 177 mass chromatograms (Brooks, 1986a). On the other hand, the C_{28} triterpane, 17α(H),18α(H),21α(H)-28,30-bisnorhopane does not commonly occur in crude oils (Rullkötter and Wendisch, 1982, Rohmer *et al.*, 1992). They have been observed to diminish in concentration with increasing maturity levels, and hence, are lower in mature hydrocarbon fluids but are more abundant in source rock bitumen and immature oils (Ekweozor *et al.*, 1979a, Ekweozor *et al.*, 1979b). Their low concentrations have been attributed to a dilution effect by more generated hydrocarbons rather than a depletion cause (Brooks, 1986a).

2.5.4. *Aromatic Hydrocarbons*

More geochemical studies have been conducted based on the saturated hydrocarbon fractions than on aromatic hydrocarbon fractions. This could be mainly due to the fact that the saturated hydrocarbons generally represent a higher proportion (>50%) of an oil or soluble rock extract, and are more responsive to the regular separation and analytical techniques (e.g. LC, GC, MS) than the aromatic compounds. (Czochanska *et al.*, 1988, Radke, 1988a). Aromatic maturity parameters, such as those derived from naphthalene and its alkyl derivatives, have been reported to be more sensitive to maturity differences in the mid to late parts of the oil generation window (Radke, 1988a). Some of these have been developed using the distributions of certain aromatic compounds in petroleum to indicate type of organic matter source input. For example, the relative abundance of specific trimethylnaphthalene (TMN) isomers (e.g. 1,2,5- and 1,2,7-TMN) identified in some Niger Delta oils have been used to support terrigenous input to their sources (Sonibare *et al.*, 2008). In an earlier, similar study, Strachan *et al.* (1988) attributed the presence of these TMN isomers to angiosperm contributions to source rock and crude oil, and further argued for their possible derivation via a disintegration of an oleanane-type triterpenoid structure.

2.6. Markers of Migration

Migration-contaminated oils have, in the past, often been interpreted as 'immature' oils due to their biomarker maturity imbalances and occurrence of unusual distributions of their components (Curiale and Frolov, 1998). Thus a better explanation for the presence of some conventional and non-conventional markers in oils will act as an aid in identifying oils that have undergone some form of modifications during migration and accumulation. Many authors have deduced migration-contamination using molecular maturity parameter imbalances due to abnormal oil biomarker distributions (Philp and Gilbert, 1986, Hughes and Dzou, 1995), most of which occur in oils trapped in Tertiary systems (Curiale, 2002). There are, however, few instances of pre-Tertiary occurrence of migration-contamination. For example, Li *et al.* (2001) suggested that pre-Jurassic-sourced oil in the Turpan Basin of China has extracted components from a Jurassic coal during migration along the coal beds.

A number of reported instances of migration-contamination agree that the olefinic hydrocarbons are the most common markers of evidence of the process (e.g. Philp and Gilbert, 1982, Ukpabio *et al.*, 1994, Curiale, 1995, Curiale, 2002). Non-hydrocarbon markers compounds also occur in petroleum, but are seldom reported, probably, due to the fact that hydrocarbons are major components in crude oil and much more commonly studied. Such non-hydrocarbon compounds as carboxylic acids, carbazole and derivatives, phenol and derivatives and ketones have been observed to show changes in their concentrations and/or distributions in petroleum as a result of migration (e.g. Jaffé *et al.*, 1988b, Larter *et al.*, 1996, Lucach *et al.*, 2002). Jaffé *et al.* (1988a) observed the solubilisation of immature organic matter during migration as one of the processes that control, to a large extent, the changes in the acidic biomarker distribution during migration. Furthermore, Jaffé and Gallardo (1993) suggested the usefulness of isomeric distributions of hopanoic acids in crude oil as indicators of migration histories. Although migration studies can provide guidance for future exploration efforts using specific molecular indicators, these need to be viewed with considerations for other important factors such as source or maturity (Jaffé and Gallardo, 1993, Curiale, 2002).

2.6.1. *Olefins: Origin and Occurrence in Petroleum*

Olefins are unsaturated aliphatic hydrocarbons usually found in thermally immature sediments and source rocks (e.g. ten Haven *et al.*, 1992, Curiale and Frolov, 1998) Geochemical studies in the past two decades have established their presence and abundance

in various crude oils (Figure 2.3) (e.g. Smirnov *et al.*, 1992, Frolov and Smirnov, 1994, Curiale, 1995, Eneogwe *et al.*, 2002). Table 2.2 shows some examples of occurrences of olefin-containing crude oils that have been reported in the literature. These petroleums have been found in reservoir rocks from pre-Cambrian through Tertiary ages (Curiale and Frolov, 1998). There are instances of specific olefin-type identification in Tertiary oils corresponding to biomarker structures (e.g. oleanenes and ursenes), while those in crude oils reservoired in pre-Tertiary rocks are mostly comprised of terminal or trans-olefins. This may be due to the limitation of certain related angiosperms contributors, such as oleanoids and ursanoids, in pre-Tertiary sources. However, establishing a clear connection between geologic time and olefin distribution could be limited, in application, by incomplete representative samples and patchy datasets such as shown in Figure 2.3.

Table 2.2 Examples of olefin-containing crude oils reservoired in rocks ranging from Precambrian to Tertiary age. The olefin concentrations in these oils are observed to generally decrease with decreasing reservoir age (extracted from Curiale and Frolov, 1998).

Age	**Location/Basin**	**Olefin Conc./ Type**	**References**
Cambrian/ Precambrian	Carbonates of Namibia	C_{11-21} n-alkenes	McKirdy et al. (1981)
Ordovician/ L.Palaeozoic	Ouachita of SE Oklahoma; Marathon of West Texas.	0.5- 7.2%wt	Frolov (1995)
Palaeozoic	Many Russian oils of varying reservoir ages	2-8%wt	Melikhov et al. (1996)
Mesozoic	Several USSR basins	Trace-10%wt	Frolov and Smirnov (1994)
	Azua Basin, Dominican Republic	Δ17,21-(C_{30-35}) Hopenes	Walters et al. (1995)
Devonian	Bradford Field, Pennsylvania;	Up to 9%wt	Hoering (1977)
	Williston Basin, Canada	Terminal olefins, trisnorhopenes	Li et al. (1997; 1998)
L.Cretaceous/Tertiary	Hammerhead oil, offshore Northeast/Slope Alaska	Oleanenes, ursenes, diasterenes	Curiale et al. (1995)
Tertiary	Several USSR oils	Trans-olefins isomers	Frolov and Smirnov (1994)
	Mesozoic-E.Cenozoic, East Kamchatka Basin, Russia	Unspecified; 1.4%wt	Bazhenova et al. (1998)
	Cook inlet Basin, Alaska (mainly Jurassic)	Trans-olefins isomers	Curiale and Frolov (1998)
	Lodo Formation, San Joaquin basin, California	Diasterenes, dammarenes	Bac et al. (1990)
	Niger Delta	Oleanenes, ursenes, diasterenes	Ukpabio et al. (1994)
	Beaufort/Mackenzie Delta	Noroleanenes, diasterenes,	Curiale (1991); Peakman et al.(1991a)
	Offshore Louisiana, Gulf Coast Basin, USA	Diasterenes, dammarenes	Curiale and Bromley (1996a)
	Kutei Basin, Indonesia	Oleanenes, bicadinenes	Curiale et al. (2005)

Since olefins are considered to lose their stability (Hunt, 1995) or be completely lost at oil generation temperatures, or corresponding maturity levels, via hydrogenation (Tissot and

Welte, 1984), their unusual presence in crude oils has resulted in the quest for their possible sources. One type of incidence entails extraction or solubilisation of organic materials from nearby shallower organic-rich immature sediments by the mobile oil (migration-contamination) during and/or after migration from source to reservoir (cf. Philp and Gilbert, 1982, Ukpabio *et al.*, 1994, Curiale, 1995). However, in exceptional documented cases, olefins could, in fact, be indigenous to the oil, where they have been observed to be source-derived, i.e. migrated, normally, from the source to the reservoir with rest of the oil (Curiale, 1995, Eneogwe *et al.*, 2002). An example of such instances is the occurrence of oleanenes and ursenes in well-known Tertiary deltaic oils such as in the Niger Delta which contain considerable amounts of these olefins. And because they generally correlate in concentration with angiosperm specific oleanane biomarkers in such oils, oleanenes and ursenes are believed to be source-derived rather than the consequence of migration-contamination (e.g. Eneogwe *et al.*, 2002). There is also a third documented proposal which supports a concept of olefin (*n*-alkene) generation in oils, particularly those of Palaeozoic and Precambrian rocks, by natural radiolytic dehydrogenation of co-existing *n*-alkanes in the earth crust (e.g. Frolov and Smirnov, 1994, Frolov *et al.*, 1996, Melikhov *et al.*, 1996, Curiale and Frolov, 1998, Frolov *et al.*, 1998). Radiolytic (non-selective) dehydrogenation is thought to be a low intensity radiolysis resulting from irradiation by natural radioactive elements such as Uranium (U), Thorium (Th), Radium (Ra), and Radon (Rn) in minerals which are associated with hydrocarbons fluids in the Earth's crust. Dehydrogenation of hydrocarbons results in the loss of hydrogen atoms from alkanes to form alkenes. Hence, a corresponding molecular weight distribution between both coexisting compounds can demonstrate this process (e.g. Frolov and Smirnov, 1994, Melikhov *et al.*, 1996, Frolov *et al.*, 1998).

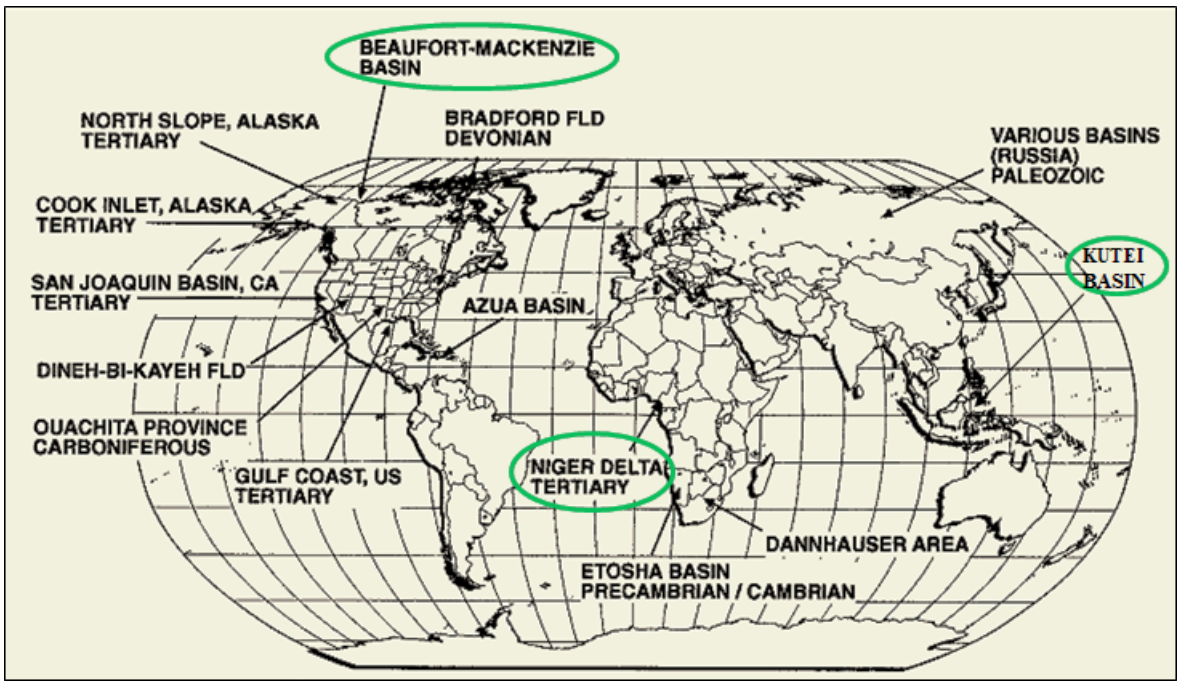


Figure 2.3 Distribution of olefins in crude oils and condensates worldwide; the locations shown contain one or more of the compound types in, at least, one oil or condensate in the basin: trans-olefins, normal olefins, oleanenes, ursenes, diasterenes, hopenes, dammarenes (after Curiale and Frolov, 1998).

A further, but uncommon, source of olefins is due to localised thermal impact induced by hydrothermal or igneous intrusive activities in accumulated oils and this has been reported in some well-known oils such as those of Dineh-bi-kayeh Field of Arizona, the Dannhauser region of South Africa (e.g. Simoneit, 1984, Bazhenova *et al.*, 1998) and certain oils of the Canadian Williston Basin (e.g. Curiale and Frolov, 1998, and references therein).

In view of the multiple possible origins of olefins in oils, consideration for interplay of various geologic factors during migration of petroleum from the point of expulsion, through its migration path, to the trap or reservoir must be given. For instance, the common belief that olefins are comparatively reactive due to their unsaturation and resultant instability at high maturity and oil generation temperatures may explain their presence in oils such as the Alaskan North Slope oil, reported by Curiale (1995). This is because the oils are generated at unusually low source temperatures and contain source-derived terrigenous olefins (oleanenes and ursenes), but lack detectable amounts of other olefins characteristic of immature organic matter (e.g. diasterenes and hopenes). However, the low temperature/low maturity theory does not apply to certain mature Niger Delta oils for which high threshold temperatures have been inferred (Ekweozor and Okoye, 1980). Curiale (1995) also argued for and against the occurrence of alkenes as migration-contamination markers in oils with consideration for consistency in their occurrence alongside other markers of source inputs, absence or abundance of other markers characteristic of immature organic matter (such as

hopenes, sterenes etc.), and the source temperature (or depth) of the oil at which it was first generated.

Occurrence of Olefin-containing Oils due to Migration-Contamination

During the process of migration, oil usually migrates from a region of high-maturity to that of a lower maturity. It is, therefore, expected that petroleum migration through an immature organic-rich system and dissolving components from it, would usually result in a migrating fluid with an apparent decreased maturity level as indicated by recognized maturity ratios (Curiale and Frolov, 1998). A similar alteration process referred to as 'reservoir overprinting' by Hughes and Dzou (1995) entails the uptake of syndepositional olefins which may be present in the immature reservoir rock by trapped hydrocarbon fluids. Olefins derived in this manner are similar, in concept, to those derived due to actual migration.

Migration-derived olefins can easily be recognised if some, or all, of the detected compounds are unstable at hydrocarbon generation temperatures. For example, the identification of key cyclic olefins in some oils of Gulf Coast Basin, USA, by Curiale and Bromley (1996a), suggests that, though oleanenes could be source-derived, the likelihood of dammarenes and diasterenes being retained at high oil generation temperatures is dismissible. Furthermore, low maturities of an apparently mature subject oil, indicated by relatively low molecular maturity parameters, are additional indicators of migration-contamination. Source-derived olefinic land plant markers such as oleanenes, in the present case study, are believed to be 'thermostable', i.e., capable of withstanding moderate degree of heat, such as oil generation temperature, without loss of their characteristic double bonds. Other documented instances of olefin occurrence (Table 2.2) in oils due to migration-contamination and in-reservoir alterations (e.g. Table 2.1) include the Niger Delta (Nigeria) oils (Ukpabio *et al.*, 1994), the Dominican Republic Azua Basin crudes with extended $\Delta^{17,21}$-($C_{30\text{-}35}$) hopenes (Walters *et al.*, 1995), the reservoired oils of Lodo Formation, San Joaquin Basin, California (Bac *et al.*, 1990).

Isolation and Detection of Olefins in Crude Oils

It has now been established that many oils contain detectable amounts of olefins, ranging from trace amounts up to 10wt% and are present in more crude oils than originally thought (Frolov and Smirnov, 1994, Smirnov *et al.*, 1994, Melikhov *et al.*, 1996, Curiale and Frolov, 1998, Frolov *et al.*, 1998). However, their detection in oils often requires the use of analytical

procedures that are not normally used for the routine analysis of saturated and aromatic hydrocarbons and this may explain the relative lack of attention that has been given to this class of hydrocarbons.

The normally very low or insignificant olefinic content in most crude oil in relation to other hydrocarbon groups has led to the use of several different methods for isolating and detecting them. As summarised in Table 2.3, olefin contents have been measured by such analytical techniques as nuclear magnetic resonance (NMR) spectroscopy, liquid (LC) and thin layer chromatography (TLC), high performance liquid chromatography (HPLC), infrared (IR) spectroscopy, gas chromatography (GC), mass spectrometry (MS), and GC-MS (e.g. Curiale and Frolov, 1998).

Table 2.3 Analytical methods, with their approximate detection limits, employed by different studies for isolation and detection of olefins in crude oils.

Isolation/ detection methods	Detection limit	Pros and cons	References
Liquid chromatography (LC)	-	Olefins are free of saturates but contain mono-aromatic HCs	Frolov and Smirnov (1994; 1990)
Thin layer chromatography (TLC)	0.5wt%	Separates olefins from monoaromatic hydrocarbons	Frolov and Smirnov (1994; 1990)
Silver ion (Ag^+) -TLC	0.05wt%	cleaner olefin fraction; small starting crude mass <0.5mg required	Frolov and Smirnov (1994)
HPLC (monitored by micro-ozonolysis of the aliphatic fraction)	0.25μmol/g	Olefin fraction contain saturates but free of aromatic HCs	Frolov et al. (1996)
^{1}H and ^{13}C NMR spectroscopy	0.5-0.8wt%	Can detect MAS components in olefin fraction	Frolov and Smirnov (1994); Melikhov et al. (1996); Smirnov et al. (1992)
Infrared (IR) spectroscopy	2-3wt%	Uses intense absorption band to identify trans-olefins	Curiale and Frolov (1998); Melikhov et al. (1996)
Gas Chromatography	-	Most common quantitative technique	Curiale and Frolov, 1998; Frolov, 1995; Melikhov et al., 1996; and many others
Mass Spectrometry	-	Useful for low concentration compounds and specific mass ions	Rullkötter et al. (1984); ten Haven and Rullkötter, (1989)

Identification and Classification of Olefins

Most olefins in oils have been shown to be monoenes (single, double bond) for carbon numbers up to thirty (Smirnov *et al.*, 1994, Frolov *et al.*, 1996). Normal alkenes, as well as

branched alkenes, have been recognised. The proportion of straight-chain, though not a major type of crude oil olefin (Smirnov *et al.*, 1994), to total olefins varies from oil to oil but their abundances often vary proportionally to those of the normal alkanes in the oil saturated fraction (Frolov and Smirnov, 1994). Various types of olefins have been identified in oils and include those shown in Table 2.2.

Olefins in crude oils can be related to their source inputs during deposition or as a function of geologic events that occurred. For example, Tertiary oils are characterised by the abundance of oleanenes, ursenes and hopenes, while suites of terminal olefins or trans-olefins have been identified in pre-Tertiary oils (Curiale and Frolov, 1998). These classifications have not been undoubtedly substantiated due to the scattered and inconsistent nature of data sets in many related studies (Curiale and Frolov, 1998).

2.6.2. *Carboxylic Acids in Crude Oils as Fatty Acids Methyl-Esters*

Carboxylic acids are major constituents of the lipids of many living organisms and they are widespread chemical fossils in petroleum and sediments (Behar and Albrecht, 1984). This complex group of non-hydrocarbon compounds constitute the major polar portion of petroleum (e.g. Jaffé and Gallardo, 1993). They have been identified in many crude oils, particularly those of Tertiary deltaic origin, at different stages of generation, diagenesis, maturation, migration, accumulation and biodegradation. Examples of isolated acid fraction of a Niger Delta crude have been documented by Schmitter *et al.* (1978), (1981) and Jaffé *et al.* (1988a) in which they observed distributions of polycyclic carboxylic acids with pentacyclic triterpenoid structures. Studies have also been carried out on the reservoired oils of Albacora field of the Campos Basin, offshore Brazil (Koike *et al.*, 1992) and oils of the Mahakam Delta, Indonesia (Jaffé *et al.*, 1988a; 1988b).

Origin of Acids in Petroleum

Although they were first discovered in crude oil over a century ago (Lochte and Littman, 1955 cited in Jones *et al.*, 2001), their presence and functions in geological samples have been relatively less studied over the past 40 years until recently (cf. Seifert, 1975, Schmitter *et al.*, 1978, Corbet *et al.*, 1980, Schmitter *et al.*, 1981, Mackenzie *et al.*, 1982, Behar and Albrecht, 1984, Jaffé *et al.*, 1988b, Jaffé and Gallardo, 1993, Nascimento *et al.*, 1999, Galimberti *et al.*, 2000, Jones *et al.*, 2001, Watson *et al.*, 2002). In their detailed study of the coals and oils of the Mahakam Delta, Indonesia, Jaffé *et al.* (1988b) proposed two processes

as being responsible for the changes in acidic biomarker distribution in the oils during migration: migration-contamination and, to a lesser extent, geochromatography. Differences in changes in the acid distributions between both processes were used to distinguish them. In addition, the increased abundance of acidic components in more biodegraded oils was believed to be a mere concentration effect due to preferential removal of other organic fractions (Behar and Albrecht, 1984) and/or a likely neoformation by a microbial-induced accumulation (Mackenzie *et al.*, 1983, Meredith *et al.*, 2000, Watson *et al.*, 2002).

Applications of Carboxylic Acid Characterisation in Crude Oils

Although carboxylic acid fractions extracted from crude oils and sediments are not frequently used in routine biomarker assessments, they have been shown to be useful in maturation (e.g. Mackenzie *et al.*, 1982, Jaffé and Gardinali, 1990) and biodegradation studies (e.g. tricyclic/hopanoic acid ratios, Behar and Albrecht, 1984, Nascimento *et al.*, 1999, Watson *et al.*, 2002) as well as in some correlation studies of mixed oils based on their abundance or depletion. The structural relationship between such polar compounds as carboxylic acid and the corresponding hydrocarbons suggests that some alkanes may partly have been derived from the acids through a proposed oxidative cleavage or decarboxylation during diagenesis and maturation (Schmitter *et al.*, 1981, Behar and Albrecht, 1984). This presents a potentially useful application for the interpretation of biomarker distributions. These compounds are known to have a significant control on the total acid number (TAN) oil acidity parameter and consequently on corrosion problems in oil refining (Meredith *et al.*, 2000, Jones *et al.*, 2001, Watson *et al.*, 2002). Their geochemical significance can be extended to complement other common biomarkers as indicators of petroleum migration (Jaffé *et al.*, 1988a, Jaffé and Gallardo, 1993).

Analysis and Identification of Carboxylic Acids in Crude Oils

Many extraction procedures and analytical methods have been used for the isolation, identification and quantification of various acid groups in oils and sediments. Some of the documented methods for the separation of carboxylic acid fractions include simple aqueous/alcoholic base extraction or saponification steps, modified KOH- or K_2SiO_3-impregnated silica gel adsorption methods, non-aqueous ion exchange-based methods including versions coupled with solid phase extraction (SPE) (Mackenzie *et al.*, 1981, Behar and Albrecht, 1984, Jaffé *et al.*, 1988b, Jones *et al.*, 2001 and the references therein,

Strelnikova *et al.*, 2005). Methyl esters of the acid fractions have been derived, prior to further analysis (e.g. GC), by various derivatisation methods such as methylation with BF_3/methanol, diazomethane and esterification with fluoroalcohols (Jones *et al.*, 2001 and the references therein). The acid methyl esters have been analysed by a number of techniques including infrared (IR) spectroscopy, gas chromatography (GC), mass spectrometry (MS) and high resolution GC-MS (Seifert and Teeter, 1970a, Behar and Albrecht, 1984, Jaffé and Gallardo, 1993). Carboxylic acids can be broadly grouped into cyclic and acyclic acids. The types of acids found in terrestrially-derived organic matter (e.g. Mahakam Delta oils) are usually a combination of types of these groups (e.g. Mahakam Delta oils, Jaffé *et al.*, 1988b). They typically, include a wide range of linear acids (C_{10}-C_{24-34}), cyclic and acylic isoprenoid acids and cyclic triterpenoic acids such as the (C_{30}-C_{32}) hopanoic acids (Schmitter *et al.*, 1978, Behar and Albrecht, 1984).

2.7.Potential Migration Markers: Non-Hydrocarbon Compounds

The role of secondary petroleum migration in controlling the composition of petroleum has received increasing attention through field and laboratory-based studies, but is still poorly understood. Many geochemical studies have collected much significant data on the saturated and aromatic hydrocarbon compounds (e.g. Li *et al.*, 1997, Galimberti *et al.*, 2000). Although the hydrocarbon-derived parameters can supply important indications about oil histories, non-hydrocarbon compounds can be an important complementary source of information since NSO-containing compounds are known to be more sensitive to migration-induced changes. This is because their high polarities mean that their abundances or distributions may be altered by rock mineral adsorption and/or dissolution processes during oil migration (Ioppolo *et al.*, 1992, Li *et al.*, 1997, Galimberti *et al.*, 2000, Lucach *et al.*, 2002). Therefore, these interactions can furnish geochemists with specific information useful for the development of models for mapping migration pathways (Larter *et al.*, 1996, Li *et al.*, 1997).

Non-hydrocarbon compounds often constitute a large fraction of oils but are seldom reported, probably, due to the fact that hydrocarbons are the major components in crude oil and are much more commonly studied (Galimberti *et al.*, 2000). Moreover, their separation and analysis are typically tedious and time-consuming with related low reproducibility results and uncertainties in their interpretations which limit their applications in petroleum geochemistry. However, there have been on-going developments on the practical use of these polar compounds as migration tracers in petroleum studies due to the growing interest

and recognition of their roles in geochemical processes (Schmitter *et al.*, 1978, Jaffé *et al.*, 1988a, Nascimento *et al.*, 1999, Galimberti *et al.*, 2000, Jones *et al.*, 2001, Taylor *et al.*, 2001, Strelnikova *et al.*, 2005). Moreover, the recent development of Fourier Transform Ion Cyclotron Mass Spectrometry (FTMS) has opened up new avenues for the characterisation of NSO compounds in petroleum and obtaining geochemical information from them, resulting in a new branch of petroleum geochemistry that has been called "petroleomics" (e.g. Marshall and Rodgers, 2004, Rodgers and Marshall, 2007).

The types of NSO compounds which have been reported in the literature include the pyrrolic (e.g. carbazole and derivatives) and pyridinic (e.g. quinoline) nitrogen compounds (Clegg *et al.*, 1998, Hwang *et al.*, 2002), and some oxygen compounds such as carboxylic acids, ketones, esters and phenols, as well as their alkyl derivatives (e.g. Ioppolo *et al.*, 1992, Jaffé and Gallardo, 1993, Larter *et al.*, 1996, Galimberti *et al.*, 2000, Lucach *et al.*, 2002, Strelnikova *et al.*, 2005). These compounds have been observed to show changes, either in their concentrations or distributions in petroleum and their routine application is believed to have great potential for enhanced interpretation of migration processes (Jaffé *et al.*, 1988a, 1988b). For example, Larter *et al.* (1996), in agreement with Li *et al.* (1995), showed that alkylcarbazole and benzocarbazole abundance and isomeric distributions are mostly maturity independent and that they undergo changes with migration distance. On the other hand, Clegg *et al.* (1998) and Li *et al.* (1997) argued that source facies and thermal maturity can have strong influences on the benzocarbazole isomer distributions and that they should not be exclusively used as migration markers. This view was also supported by Hwang *et al.* (2002) who suggested that the impact of maturity and source facies on the distributions be first considered and minimised in order to successfully apply these compounds as migration tools. Likewise, the distribution and partitioning behaviours of phenols derivatives in crude oil has also been demonstrated as useful or potential tool for establishing oil migration in certain depositional settings (Bennet and Larter, 1997, Taylor *et al.*, 1997, Galimberti *et al.*, 2000, Lucach *et al.*, 2002). Although some of these earlier studies have debated the suitability of some non-hydrocarbon compound parameters as migration indicators, it has been reported that there are still good prospects for their routine application to petroleum migration problems (Galimberti *et al.*, 2000).

Chapter 3 Methodology

3.0.Outline

This chapter describes the methods and techniques applied in this project. Figure 3.1 is a schematic of the overall project design. Two sets of samples are studied and these include a set of field samples consisting thirty three crude oils and a set of the laboratory samples consisting of twenty four (in duplicate) crude oil eluates resulting from a laboratory oil migration experiment.

The approach involves the analyses of samples for the distributions of specific hydrocarbon and non-hydrocarbon markers. Emphasis is on the abundance and distribution of unsaturated aliphatic hydrocarbons (olefins) and carboxylic acids. Four major compound classes: the saturated, unsaturated (olefinic) and aromatic hydrocarbons, and the carboxylic acids were analysed in nearly all the samples.

Open column (glass) liquid chromatography was initially employed to obtain the hydrocarbon (aliphatic and aromatic) fractions. The aliphatic fractions were subjects for olefin isolation by TLC and Ag^{+}-TLC methods. Compositional analysis of all obtained analyte fractions were carried out by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) to determine the distributions and concentrations of specific biomarkers.

A non-aqueous ion-exchange method as described by Jones *et al.* (2001) was used to isolate carboxylic acids from the oils and extracts. The resulting replicate methylated acidic fractions underwent GC and GC-MS analysis for identification and quantitation of the acids as their methyl ester derivatives.

Simulated migration experiments were carried out in the laboratory with a mature, marine-sourced North Sea crude oil and an organic-rich immature Kimmeridge shale (Blackstone) using a High Performance Liquid Chromatography (HPLC) column set up. Collected aliquots of ‘migrated’ oils were then subjected to similar analysis as the crude oils to determine any compositional changes.

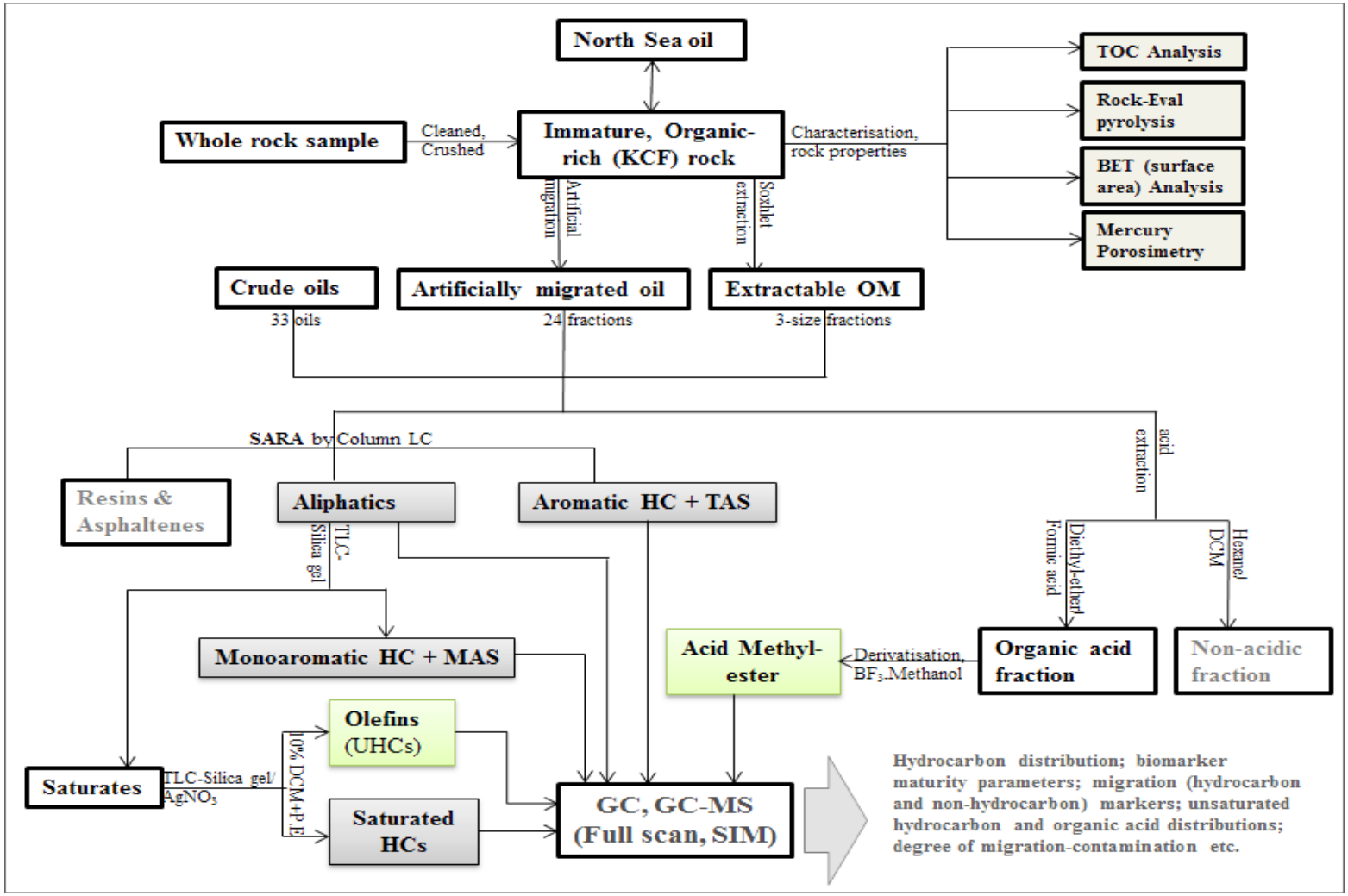


Figure 3.1 Schematic flow of the project methodology.

3.1. General Experimental Procedures

All solvents used during laboratory procedures were redistilled in an all-glass system. Silica gel, alumina and cotton wool for chromatography were extracted with azeotropic 97:3 Dichloromethane-methanol solvent mixtures for 24 hours using a Soxhlet apparatus. The set-up comprised 500 ml round bottom flasks containing the extracting solvent with a few anti-bumping granules, clean cellulose thimbles (containing the material to be extracted and plugged with extracted cotton wool) and the Soxhlet extractor. Both the silica gel and alumina were reactivated in an oven at 120^{o}C for at least 2 hours prior to each use.

All glassware and vessels were washed in detergent solution followed by rinsing in distilled water. These were then dried in an oven at 60^{o}C and allowed to cool; they were rinsed with dichloromethane (DCM) before use. New, clean glass pipettes were used for each sample/fraction to minimise the incidence of cross contamination. Precautions were taken to avoid all contacts of the samples with plastics and bare fingers. All other relevant precautions for specific analytical techniques were taken to minimise analytical errors and sample contamination.

COSHH risk assessments of the procedures used were carried out and appropriate personal protective equipment worn at all times during laboratory procedures.

3.2. Samples

Three sample sets were used in this study:

- 33 crude oils from 4 different petroleum provinces, mainly Tertiary deltaic ones;
- 3 different particle-sized fractions of pulverised Kimmeridge Blackstone and;
- 48 (2x 24) ‘migrated’ eluates from a laboratory-simulated migration experiment.

The field sample set is comprised mainly of Tertiary deltaic (terrigenous) crude oils, since these are the types of oils that are often reported to suffer from migration contamination (see Chapter 2, section 2.2), while the other oils (5) represent oils of predominantly Jurassic Type II, marine origin, and have been used in this study as controls for some specific biomarker- and geological setting-based assumptions. Table 3.1 shows a list of all the crude oils investigated in this work and their locations. The oil samples were available from the School (CEG, Newcastle University) geochemistry laboratory.

Table 3.1 List of all crude oil samples studied in this work.

Sample name	Region	Basin/ Field	Country
BMD01	Beaufort - Mackenzie		Canada
BMD02	Beaufort - Mackenzie		Canada
BMD03	Beaufort - Mackenzie		Canada
BMD04	Beaufort - Mackenzie		Canada
BMD05	Beaufort - Mackenzie		Canada
CAN06	Beaufort		Canada
CAN07	Beaufort		Canada
CAN08	Beaufort		Canada
KTM01	Kutei	Mahakam Delta	Indonesia
KTM02	Kutei	Mahakam Delta	Indonesia
KTM03	Kutei	Mahakam Delta	Indonesia
NDE01	Niger Delta-	East	Nigeria
NDE02	Niger Delta	East	Nigeria
NDE03	Niger Delta	East	Nigeria
NDE04	Niger Delta	East	Nigeria
NDE05	Niger Delta	East	Nigeria
NDE06	Niger Delta	East	Nigeria
NDE07	Niger Delta	East	Nigeria
NDE08	Niger Delta	East	Nigeria
NDW09	Niger Delta	West	Nigeria
NDW-10	Niger Delta	West	Nigeria
NDW11	Niger Delta	West	Nigeria
NDW12	Niger Delta	West	Nigeria
NDW13	Niger Delta	West	Nigeria
NDW14	Niger Delta	West	Nigeria
NDW15	Niger Delta	West	Nigeria
NDC16	Niger Delta	Central	Nigeria
NDC17	Niger Delta	Central	Nigeria
TRO01	Oropouche	SouthWest Peninsula	Trinidad & Tobego
NSA02	A2	North Sea	UK
NSA03	A3	North Sea	UK
NSA04	Not known	North Sea	n/a
NSV05	Veslefrikk	Northern North Sea	Norway

The crude oil used for the migration experiment is a Jurassic Type II marine North Sea oil similar to one of the reference oils, NSA03, used in this study, from which migrated eluates/fractions were obtained; the solid phase in the experiment was immature, organic-rich Kimmeridge Blackstone collected from an outcrop on the Dorset area of the Kimmeridge Clay Formation (KCF), described later in this chapter. This was representative of immature organic matter in some migration pathways that could give rise to migration contamination.

The reference oils are dominantly marine-sourced and are believed not to have migrated through immature organic-rich carrier beds, and hence are not expected to have suffered from migration-contamination. Two of the reference oils are of mixed (marine/terrestrial) origins and are also important as their compositions can be expected to show mixed attributes of both marine and terrestrial sourced oils in respect of their molecular marker contents.

3.2.1. *Sample Storage*

The crude oil samples were stored at room temperature in metal cans with tightly fitted lids. The stability of some analytes such as the olefinic fractions was maintained by storage in a refrigerator until ready for further analysis. Bottled and prepared standard solutions were stored in the fridge or freezer as required for their preservation.

3.2.2. *Recovery Standards and Sample Preparation*

In order to assess analytical reproducibility, many of the analyses were carried out as replicates, together with procedural blanks, to check for any contamination.

Four recovery standards were selected as a pair of surrogate and internal standards for saturated and aromatic hydrocarbons. Standard solutions of squalane and 1, 1'-binaphthyl were prepared and known amounts were initially added to each of the weighed oil aliquots for analysis, as saturate and aromatic hydrocarbon recovery standards, respectively. Standard solutions of internal standards were also prepared and added to the samples prior to GC/GC-MS analyses. Details of the quantities are given in following section. A complete list (table) of all standards that were used in this study, and their sources are shown in Appendix I-a.

3.2.3. *Weights Used*

Aliquots of approximately 50-60 mg of each oil sample were accurately weighed for analyses. All standard solutions were prepared individually in 25-50 ml volumetric flasks. An amount of squalane equal to 0.5% by weight of the oil aliquot used was added to the oil samples. This was taken from a standard solution of 2 mg/ml DCM concentration which was made up by weighing 100 mg of squalane into a clean 10 ml vial. This was slightly diluted, and was then transferred into a clean volumetric flask. Similarly, an amount of 1,1'-binaphthyl equal to 0.125% by weight of the oil aliquot used was also added to the oil samples. A standard solution (1 mg/ml) of 1, 1'-binaphthyl was prepared by dissolving 50

mg of solid standard in DCM in a 50 ml volumetric flask. The amount of standard, by weight, to be added to any hydrocarbon analyte solution was derived using its fraction of whole sample taken for hydrocarbon analysis by GC and GC-MS. Hence, for a quarter aliquot (analyte) of a 50 mg sample containing 250 µg squalane, approximately one-quarter (by weight) of squalane amount (~ 62.5 µg) was added.

3.3. Experimental Techniques

3.3.1. *Isolation of Hydrocarbons*

The steps used in the separation of the hydrocarbon classes of interest in this work are shown in Figure 3.2. The total petroleum hydrocarbons (TPH) fractions of the sample containing mainly the aliphatic and aromatic hydrocarbons were separated into aliphatic and aromatic fractions. The aliphatic fractions were subjected to further separation to yield the saturated and unsaturated hydrocarbon (olefin) fractions.

Open Column (Liquid) Chromatography

Extracted and activated chromatography grade silica gel and alumina (Brockman grade 1, Merck, UK), were used for the separations. The LC glass columns (25 cm length, 0.8 cm ID) were fitted with a small plug of cotton wool to retain the adsorbents and slurry packed to two-thirds of the column length with silica gel in petroleum ether. A bed (~0.5 cm deep) of alumina was placed on top of the silica gel.

Approximately 50 mg aliquots of each of the samples were accurately weighed and, after addition of surrogate standards, were adsorbed onto activated alumina (~3 g). After all traces of used solvent (DCM) was completely eliminated by blowing the adsorbed sample under a gentle stream of nitrogen gas, the sample was then added to the top of the column, and fractionated to give an aliphatic hydrocarbon fraction by elution with petroleum ether (70 ml) and an aromatic hydrocarbon fraction with 70 ml DCM /petroleum ether (1:4). In cases where whole total petroleum hydrocarbon (TPH) fractions were required, both eluates were collected. Procedural blank analyses were also carried out.

All fractions were concentrated to about 1 ml using a rotary evaporator and where required, the fractions were further concentrated to smaller volumes under a gentle stream of nitrogen gas.

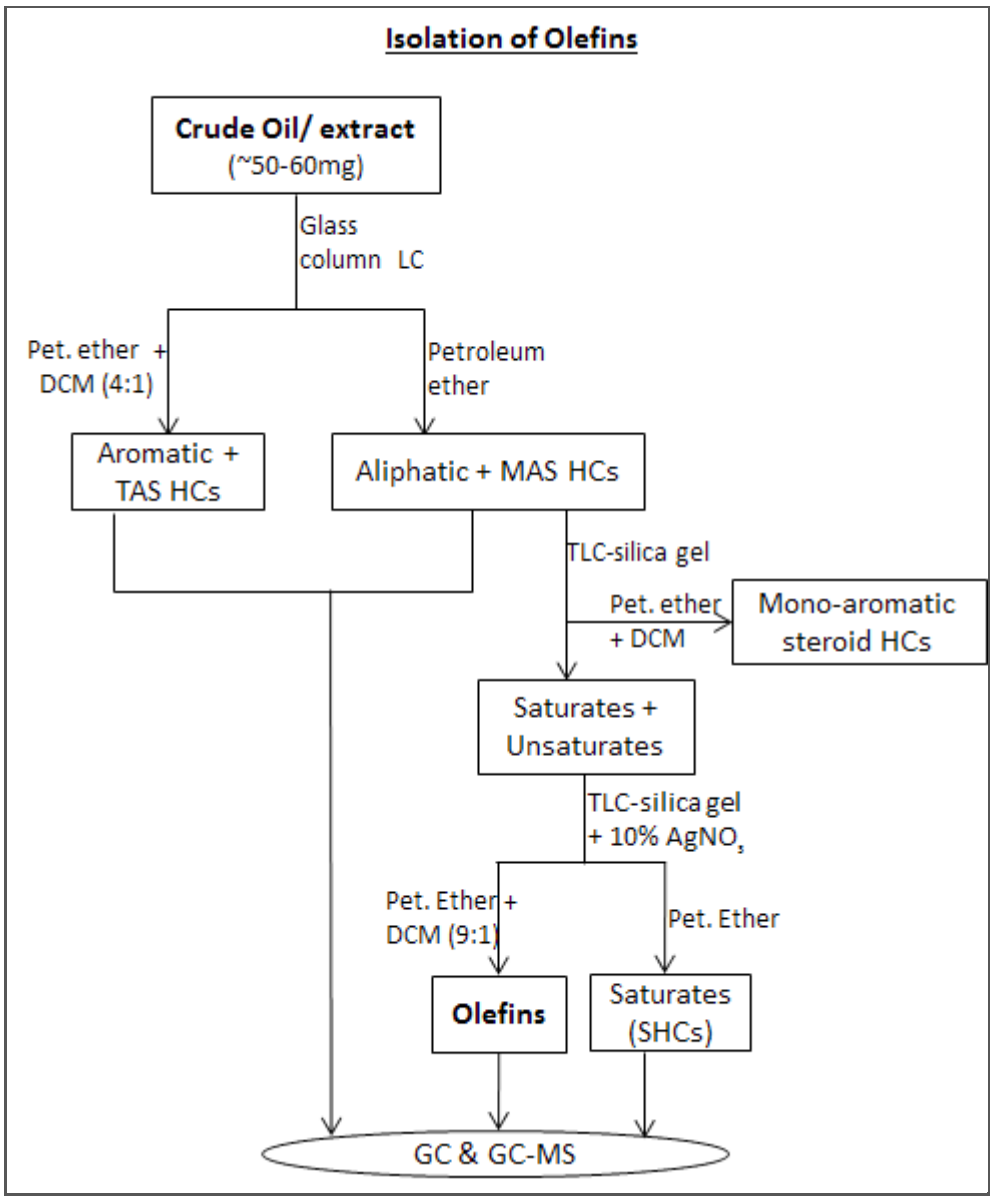


Figure 3.2 Schematic showing the isolation of olefinic and saturated hydrocarbons from whole oils.

Saturated and Aromatic Hydrocarbons

The aliphatic hydrocarbon fraction contained the saturated, monoaromatic and any unsaturated hydrocarbons. An aliquot (about a quarter) of the aliphatic fraction was taken for analysis by GC and GC-MS, while the remaining fraction was set aside for further (TLC) analysis. Whole aromatic fractions were analysed by GC and GC-MS.

3.3.2. *Isolation of Olefinic Hydrocarbons*

Unsaturated (olefinic) hydrocarbon fractions were isolated as shown in Figure 3.2.

Thin Layer Chromatography (TLC)

Monoaromatic hydrocarbons present in the aliphatic hydrocarbon fractions were first separated using the basic silica gel TLC technique. This step was necessitated due to the very low concentrations of olefins in crude oil and, more importantly, by likely interference of the monoaromatic (MAS) components.

Glass TLC plates (20 cm by 20 cm) were coated with 0.5 mm thickness silica gel (Kieselgel-60G by Merck, UK) using a slurry mix of the solid (35 g) in 70 ml distilled water, for a 5-plate set. The plates were left to air-dry for about 30 min, and then placed horizontally in a plate rack and left to activate in an oven overnight at 120^{o}C. The activated plates were cleaned before use by development in DCM and then reactivated in the oven for about two hours.

The samples for TLC separation were concentrated to ~200 µl under a nitrogen gas stream and spotted, using Pasteur pipette, in a line on the prepared TLC plate about 3 cm from the bottom of the plate. Two spots of the reference standard mixture were carefully placed, centred on a lane of the plate separated from the rest of the plate by scored lines. The standard mix contained aliphatic (squalane), mono-aromatic (n-tridecylbenzene) and aromatic (anthracene) hydrocarbons, with a concentration of about 10 mg of each component, all dissolved in ~1 ml DCM.

The spotted plates were lowered into TLC developing tanks containing about 200 ml light petroleum (petroleum ether; b.p.: 40-60^{o}C) as developing solvent. Once the solvent migrated near to the top of the initially marked solvent front from the cleaning stage, the plates were removed and allowed to dry.

Detection of the saturates (+olefins) band was done by visualising the TLC plate under UV light after treating the plate with a spray of Rhodamine-6G in methanol solution, and comparing bands of separated components with those in the reference standard mix which were eluted alongside the analyte samples. The saturates-olefins region was confirmed by the appearance of a distinct yellow band region. The lower mono-aromatic band usually showed a lighter yellow colour. Taking precaution against cross contamination, the respective areas were marked and carefully scraped into clean aluminium foil and properly labelled.

The separated saturated (plus unsaturated) hydrocarbon and the mono-aromatic hydrocarbon fractions were each desorbed in elution tubes (~15 cm long, 1.5 cm ID), plugged with cotton wool and about 1 cm bed of alumina, with 30 ml petroleum ether and DCM mixes in the ratios 1:9 and 1:4, respectively. These were concentrated to 1 ml on a rotary evaporator. The monoaromatic fractions were transferred to GC vials ready for GC and GC-MS analysis. The saturated (plus unsaturated) hydrocarbon fractions were prepared for further TLC (argentated) separation.

Ag^+ TLC-Silica gel method of olefin separation

Silver nitrate ($AgNO_3$) impregnated silica gel TLC was used to separate saturated from unsaturated hydrocarbon fractions (cf. Frolov and Smirnov, 1994). Similar procedures as earlier described for TLC-silica gel plates are also applicable here except that 3.5g of silver nitrate (corresponding to 10% of the weight of silica gel used) was first dissolved in the distilled water used to make up the slurry for the plates, and stricter safety precautions were taken due to this additional factor. Also, exposure of the plates to direct light during their preparation was minimised in order to avoid the oxidation and blackening of the plates due to the photosensitive $AgNO_3$.

A reference standard mix was used to aid the detection of separated olefin TLC bands. This was a mix of ~10 mg each of *n*-eicosane ($C_{20}H_{42}$) and 1-tetradecene in ~1 ml of solvent. The plates were pre-cleaned with DCM; samples were applied and separated as described previously. Desorption procedures were the same as those described previously. The saturated hydrocarbons and the olefins were eluted off the silica gel with 30 ml petroleum ether and 30 ml (1:9) DCM/petroleum ether mixture, respectively. These were then transferred into GC vials and prepared for GC and GC-MS analyses.

3.3.3. *Analysis of Carboxylic Acids*

The procedures entailed the isolation of carboxylic acid fractions from crude oil samples, rock extracts and other oil sub-samples obtained from procedures within this project and their subsequent GC and GC-MS analyses (Figure 3.3). The following sections describe these procedures, which were based on those described by Jones *et al.* (2001).

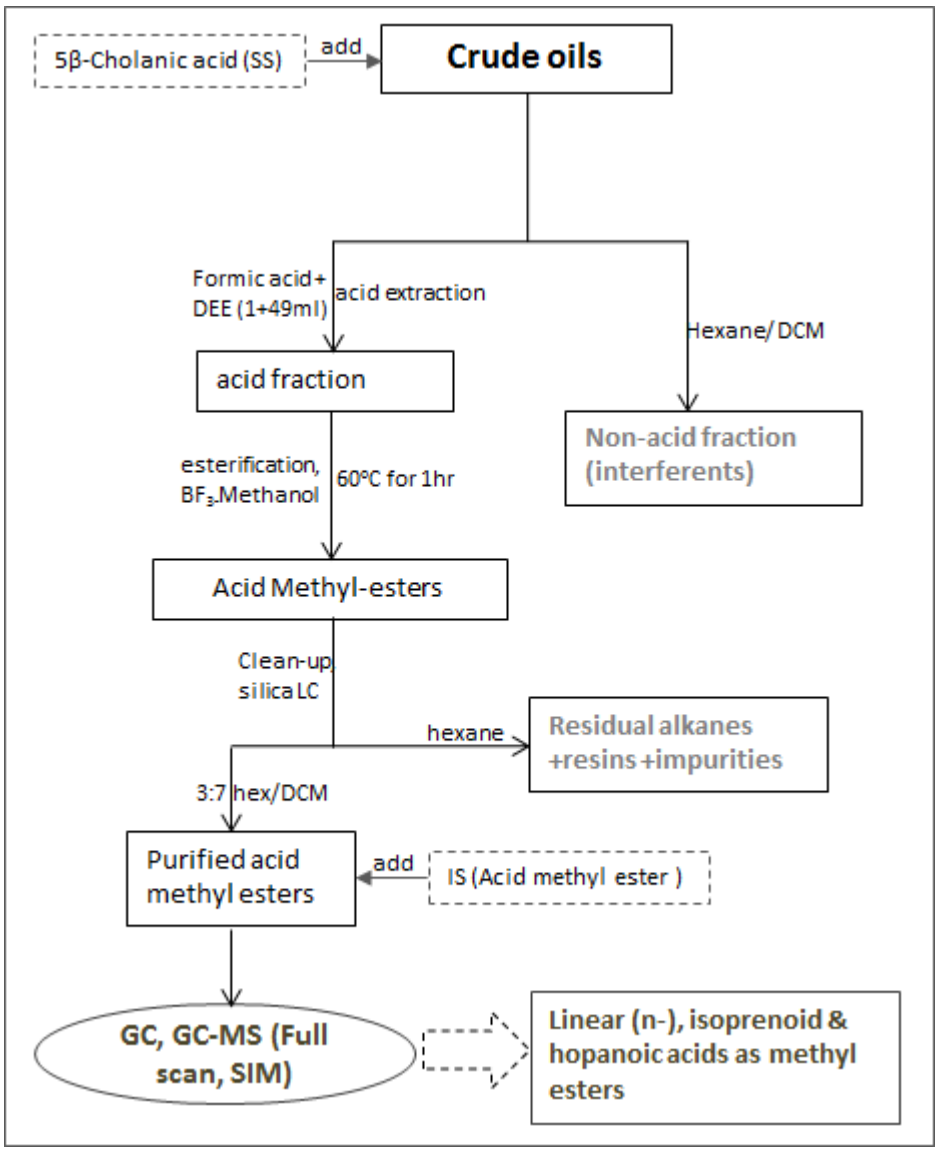


Figure 3.3 Analytical schemes for the extraction of acids from crude samples. SS = surrogate standard; DEE = diethyl ether; DCM = dichloromethane; IS = internal standard (1-phenyl-1-cyclohexanecarboxylic acid methyl ester).

A surrogate standard solution (1 mg/ml) was prepared using 5β-cholanic acid (Sigma-Aldrich UK, Ltd). The internal standard, methyl ester of 1-phenyl-1-cyclohexanecarboxylic acid, was prepared in the laboratory by methylation (BF_3-methanol) of 1-phenyl-1-cyclohexanecarboxylic acid (Sigma-Aldrich UK, Ltd). The resulting methylated fraction was subjected to liquid column chromatographic purification by elution with 100 ml of a hexane/DCM mix (60:40). Calculated yield was 60.7%.

A standard solution of the resulting sweet smelling, clear viscous liquid was first made up to 2 mg/ml dichloromethane in a 10 ml volumetric flask. An aliquot of this was analysed by GC-MS to check the purity of the clean product (Figure 3.4) which was approximately >95%.

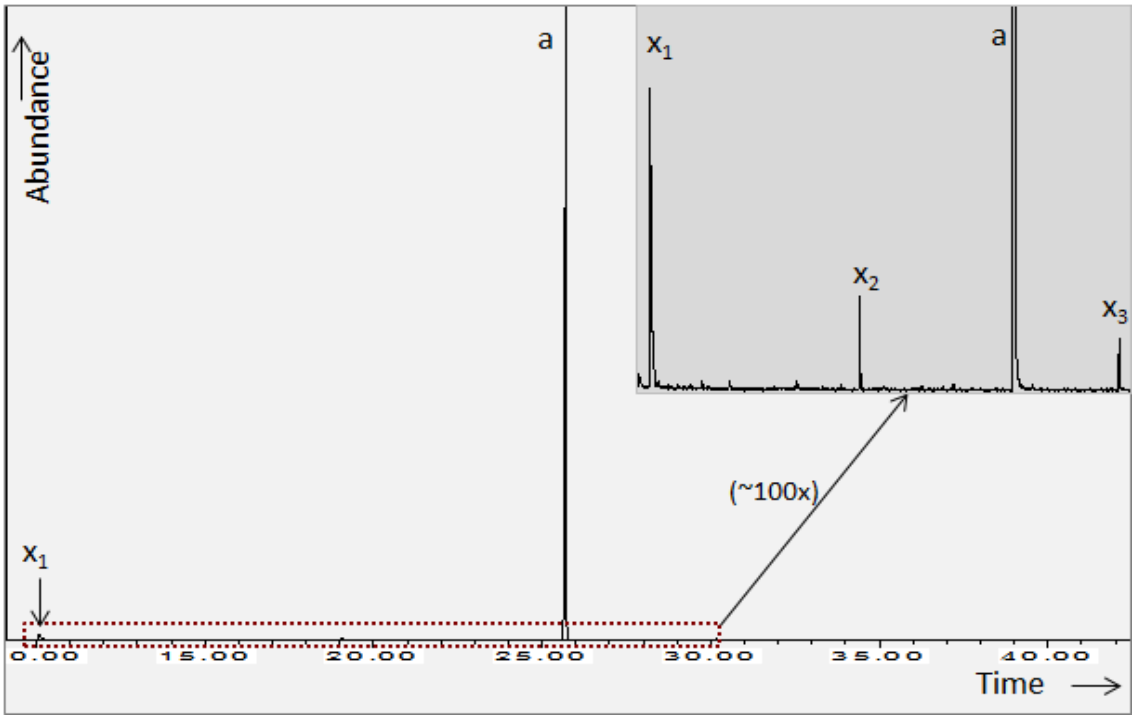


Figure 3.4 Partial chromatogram showing high purity (estimated >95% based on GC) methyl ester of 1-phenyl-1-cyclohexanecarboxylic acid (a) prepared in the laboratory. Peaks x_1, x_2, and x_3 are the next prominent, unknown peaks (impurities) whose areas' sum is negligible compared to peak 'a'.

A full list of all materials used in carrying out the acid extraction and analysis is located elsewhere in Appendix I-b. The anion exchange method of extracting carboxylic acids from hydrocarbon samples used silica-based strong anion exchange sorbent solid phase extraction (SAX-SPE) columns (Jones *et al.*, 2001).

The 6 ml glass SAX-SPE columns containing 4 g of the SAX phase (Biotage Ltd.) were fitted with glass reservoirs, and were first conditioned with 10 ml hexane followed by 10 ml hexane/DCM mixture (1:1) and then dried with an air flush using a syringe and an adaptor.

The samples were grouped for extraction procedure in batches of 5-6 samples with an additional procedural blank per batch. Between 150 mg for degraded oils (~4 case study oils) and 400 mg for undegraded samples was accurately weighed into 10 ml glass vials. Due to their thickness, the rock extracts were regarded as 'degraded oils' for the purpose of acid analysis measurements only. 10 µl of the prepared recovery standard (1 mg /ml 5β-Cholanic acid in DCM) solution was added to each sample and the blank. In the case of very thick samples, dichloromethane was used to dilute the samples prior to application.

Samples were carefully applied to the top of the preconditioned 4 g SAX quaternary amine SPE columns using glass pipettes. Interferents (non-acid compounds) were first removed by elution with 20 ml, 1:1 mix of hexane and DCM; followed by 25 ml DCM. Once the elution

of interferents was completed, the columns were air-flushed and the tips of the columns rinsed with hexane and DCM. All of the unwanted eluates were discarded.

The acids were then eluted with 2% (by volume) formic acid in 50 ml diethyl ether. The acid eluates were rotary evaporated down to 1 ml and transferred, with DCM washings, into clean 10 ml vials. These were blown down under gentle nitrogen gas stream to complete dryness and left overnight in the fume cupboard until all traces of formic acid had evaporated. After washing down the sides of the vial with DCM, the fractions were stored in a refrigerator, prior to the next stage.

The dried acid fractions were re-dissolved in DCM (1 ml) and boron trifluoride-methanol (BF_3-methanol) solution (1 ml) was then added to each of the sample solutions. The vials were shaken gently, capped with aluminium foil, placed on a metal vial rack and heated in GC oven at ~60^{o}C for 1 hour. After cooling, the samples were transferred into Quick-Fit test tubes, with DCM washings, and then 3 ml petroleum ether and 10 ml distilled water were also added. The test tubes were stoppered and shaken vigorously for about 15-20seconds, and then left to stand for 5-10 minutes. The top (organic/petroleum ether) layer containing the derivatised acids was pipetted off into clean 10 ml vials. The petroleum ether extraction was repeated 2 more times to ensure maximum recovery of the methylated acids. The water layers were discarded. The samples solutions were blown down to dryness under nitrogen.

The methylated acid fractions were purified using silica LC columns. 1 g silica SPE columns (Biotage) were conditioned with 5 ml hexane and dried with an air flush. The samples were then eluted with 4 ml hexane as follows: 0.5 ml hexane was used to re-dissolve the samples in 10 ml vials. These were capped with aluminium foil and sonicated for 5 min. The samples were then applied to the top of the columns using pipettes. The sonication and sample-column application routine was repeated twice more using 0.5 ml hexane to re-dissolve the sample each time. The remaining 2.5 ml of hexane was used to elute residual-alkanes. The columns were air-flushed after elution and the tip of the columns were rinsed with hexane and DCM.

The methylated acids retained by the silica, were eluted with 10 ml hexane/DCM (3:7) mixture into clean 10 ml vials. The samples were blown down to small volumes, and transferred to 2 ml GC vials with 300 µl inserts together with 10 µg of the internal standard-acid methyl ester and then made up to 200 µl with DCM prior to GC/GC-MS analysis.

3.3.4. *Gas Chromatography (GC)*

Gas chromatography analysis of saturated, olefinic, monoaromatic and polyaromatic hydrocarbon fractions, and acid methyl ester fractions were performed on an Agilent 5890A instrument equipped with a split/splitless inlet with tapered glass liner and a flame ionisation detector (FID). The analyte fractions, dissolved in either hexane or DCM, were injected (1 µl) onto the GC column in a split/splitless mode (30 ml/min split, 1 min. splitless) using a HP 7683B automatic injector. Separation was performed on an HP-5 coated (0.25 µm film thickness) fused silica capillary column (30 m x 0.25 mm ID). The inlet and detector temperatures were 280^{o}C and 310^{o}C respectively. Hydrogen was the carrier gas with an initial flow rate of 1 ml/min at a constant pressure of 50 kPa. The oven temperature was set initially at 50^{o}C and held for 2 min, then ramped at 5^{o}C/min to 300^{o}C and held at this temperature for 20 min. Data were acquired and processed using Thermo Atlas software and stored on the lab data system.

3.3.5. *Gas Chromatography-Mass Spectrometry (GC-MS)*

Gas chromatography-mass spectrometry (GC-MS) analyses of all fractions were performed on an Agilent 6890A GC equipped with a flame ionisation detector (FID) and pulsed splitless mode injector (280°C), and linked to an Agilent 5975C MSD (electron voltage 70eV, source temperature 230°C, quadrupole temperature 150°C multiplier voltage 1800V, interface temperature 310°C). The acquisition was controlled with Chemstation software. Samples were either analysed in scan mode (50-550 atomic mass units/second) or in selected ion monitoring (SIM) mode (30 ions; 35 ms/ion dwell). 1 µl of the analyte solution in dichloromethane was injected by an HP7673B auto sampler and the split opened after 1 minute. After the solvent peak had passed, the GC temperature programme and data acquisition commenced.

Separation was performed on an Agilent fused silica capillary column (30 m x 0.250 mm x 0.25 µm ID) coated with 0.25 µm thickness of phenyl-methylsiloxane (HP-5MS) phase. The GC was temperature programmed from, and first held at initial temperature of 50^{o}C for 2 min; then ramped at 5°C/min to 310^{o}C and held at this final temperature for 21 min with helium as the carrier gas (flow rate ~1 ml/min, initial pressure of 52.76 kPa, split at 30 ml/min). Total run time was 75 min. The acquired data was stored on PC-based lab data system for later data processing and integration. Peaks were identified and labelled after

comparison of their mass spectra with those in the literature or the NIST05 library if ≥80% fit, and their elution order agreed with published data.

The GC and GC-MS conditions used to analyse carboxylic acids (as methyl esters) were the same as described above for other hydrocarbons. Hopanoic acid concentrations were measured by comparison of their peak areas in the m/z 191 (m/z 235-C_{30}, 249-C_{31}, 263-C_{32}) mass chromatograms with that of the 5β-cholanic acid standard in the m/z 217 chromatogram assuming that response factors are equal. The GC-MS analysis was carried out in scan mode only for the acid fractions. Peak identification and data analysis were done by extracting mass ions of acids groups of interest from their total ion chromatograms (TIC).

The ions for the GC-MS selected ion monitoring (SIM) mode analysis of the saturated hydrocarbon components were: m/z 85 (*n*-alkanes and isoprenoid alkanes), m/z 163 (bisnorhopanes), m/z 183 (acyclic isoprenoids), m/z 191 (triterpanes), m/z 217 (regular steranes), m/z 231 (methyl steranes), m/z 253 (mono-aromatic steroid HCs), m/z 259 (diasteranes), m/z 386 (C_{28} steranes) and m/z 412 (C_{30} triterpanes).

For unsaturated hydrocarbons (olefins), they were: m/z 55 (*n*-alkenes), m/z 69 (isoprenoid alkenes and squalene), m/z 97 (*n*-alkenes), m/z 203 (pentacyclic terpenes), m/z 204, 205, 218 (oleanene isomers, ursenes), m/z 215 (sterenes), m/z 245 (5α-androstane standard), m/z 257 (diasterenes), m/z 271 (methyl diasterenes) and m/z 367 (hop-17(21)-enes).

The monitored ions for aromatic hydrocarbons were as follows: m/z 128, 142, 156, 170, 184 (naphthalenes), m/z 178, 192, 206 (phenanthrenes), m/z 184, 198, 212 (dibenzothiophenes), m/z 230 (*p*-terphenyl internal standard), m/z 253 (1,1'- binaphthyl surrogate standard), m/z 154, 168 (biphenyls), m/z 166, 180 (fluorenes), m/z 231 (triaromatic steroidal hydrocarbons).

3.3.6. *Analyte Quantitation using Standards*

For quantitation of aliphatic and aromatic hydrocarbon components in crude oil samples, recovery (or surrogate) standards of squalane (0.5% w/w oil) and 1,1'-binaphthyl (0.125% w/w oil) were added to oil aliquots before analysis. Internal standards, at similar concentrations to those of the surrogate standards remaining in the fractions (taking into account any aliquotting) were then added to the separated hydrocarbon fractions just prior to analysis by GC or GC-MS. For saturates, internal standards of *n*-heptadecylcyclohexane or 5α-androstane were used, and for the aromatics, *p*-terphenyl was typical. For the

unsaturated hydrocarbon (olefin) fractions, internal standards of cis-2-methyl-7-octadecene and 5α-androstane were added for quantitation of linear and cyclic alkenes respectively. The amounts of these added was generally very small (low µg) and depended on the relative abundance of the olefins in the particular sample. In order to determine an appropriate amount of standard to be added to each sample, aliquots of a few representative samples without internal standards, were first analysed GC in the same batch as a diluted pure standard of known concentration. The response or peak height of the analyte largest (olefin) peak on the gas chromatogram was compared to that of the standard peak. A simple calculation was used to estimate the amount of the largest alkene peak that corresponded to the response of the standard peak of known concentration. The amount of standard to be added to the samples was then adjusted accordingly for all the samples with varying olefin abundances.

The GC or GC-MS peak areas of analytes and any associated recovery standards were integrated either automatically or manually, depending on the concentration or detection limit for the class of compounds in question. The amounts of individual components were computed using response factors (RF), relative response factors (RRF) and percentage recovery figures derived from analyte peak areas and those of the added internal and surrogate standards.

Response factors and relative response factors can be measured using a synthetic mix containing known concentrations of each compound of interest, together with an identified internal standard. Here, if two components are incorporated at similar concentrations (X_{wt}), with internal standard at a concentration, IS_{wt}; and assuming the response index of the detector to be unity, then,

$$\frac{X_{wt}}{IS_{wt}} = \left(\frac{X_A}{IS_A}\right) X_\Psi$$

Equation 3.1 Relationship between analyte and Internal standard quantities.

Where:

- X_A = peak area of component;
- IS_A = peak area of internal standard, and;
- X_Ψ is the response factor, RF, for the component (X).

The RF (X_Ψ) for a component of any analyte can be calculated by the following;

$$RF = \left(\frac{X_A}{X_{wt}}\right)$$

Equation 3.2 Response factor (RF) of analyte, X.

However, when weighed amount of standard is now added to a sample and analysed, then the concentration of any identified component, X_{wt}, in the mixture can be calculated thus:

$$X_{wt} = \left(\frac{[X_A \times IS_{wt}]}{IS_A}\right) X_\Psi$$

Equation 3.3 Concentration of analyte component, X-(a).

Where:

- IS_{wt} = concentration or weight of the internal standard;
- X_A = peak areas of the components X;
- IS_A = peak area of the internal standard and;
- X_Ψ is the RF of components calculated using Equation 3.2.

In order to avoid the determination of RF for each component, a more practical technique of running a standard sample before, midway through and after a batch of samples was applied. In the case where no standards were added prior to experimental procedures and only internal standards were added prior to gas chromatography, RF is assumed to be unity. Then, by simple substitution in Equation 3.3, the amount of component X_{wt} was calculated thus:

$$X_{wt} = \left\{\frac{(X_A \times IS_{wt})}{IS_A} \times \frac{1}{f}\right\}$$

Equation 3.4 Concentration of component X-(b).

Where '*f*' is the fraction of the weighed sample that has been analysed.

3.3.7. *The Relative Reference Factor (RRF) Method*

The aliphatic and aromatic components and carboxylic acids data analysis was generally performed by this method. The chosen reference standards were analysed separately from the sample. During sample preparation, prior to GC analysis, a third vial containing approximately 100 µg each of all 4 recovery standards was made up to 1 ml with DCM and run on the GC and GC-MS. Here, column conditions were maintained at constant for the study samples and standard mixes.

In order to reduce the effects of any changes in the equipment's operating conditions, the analyte and standard mix solutions were run interchangeably. Furthermore, the reference standards were made up with concentrations similar to those of the sample components; this action is thought to significantly minimise errors that may arise due to slight detector changes and deviations. Data from the reference chromatograms were used for calculating results of each component. This method eliminates the need for estimating RFs for individual components and allows the derivation of a response index which compares response factors of the entire reference standards relative to one another and the detector. If RRF, in the case of analyte and internal standard, is given by the expression:

$$RRF = (X_\Psi | IS_\Psi) = \left(\frac{(X_A/X_{wt})}{IS_A/IS_{wt}}\right)$$

Equation 3.5 $RRF_{A/IS} = RF_{Analyte}/ RF_{I\text{-}Std}$.

Where:

X_Ψ and IS_Ψ are the RF of the analyte and the internal standard respectively.

Hence, the relative response factor (RRF) of the reference standards was computed using the equation:

$$RRF = \left(\frac{SS_{A-mix}}{IS_{A-mix}}\right) \times \left(\frac{IS_{wt-mix}}{SS_{wt-mix}}\right)$$

Equation 3.6 Relative response factor based on the internal and surrogate standards.

Where:

- SS_{Amix} = peak area of surrogate standard in the mix;
- SS_{wtmix} = weight of surrogate standard in the mix;
- IS_{Amix} = peak area of internal standard in the mix, and;
- IS_{wtmix} = weight of the internal standard in the mix.

3.3.8. *Correction Factor- % Recovery*

The relative response indices are usually expected to be near unity; but where this is not the case, a correction factor is calculated to offset any loss of the sample components during experiment and analysis. This is based on the principle that when a sample mixture containing known amounts of standards experiences loss during experimental procedures,

both the components and standards are lost in equal proportions. The RFs of known concentrations is virtually constant and this is proportional to the amount of component per unit sample weight. Therefore the relative response factor is proportional to the recovery of the standards in the samples, which in turn is equivalent to the efficiency of the separations of the sample components of focus. The relationship is depicted in the following equation:

$$\%Rec = \left\{\left(\frac{SS_{Ax}}{IS_{Ax}}\right) \times \left(\frac{IS_{wtx}}{IS_{wtx}}\right) \times \left(\frac{1}{RRF}\right) \times \left(\frac{1}{f}\right)\right\} \times 100$$

Equation 3.7 %Recovery assuming RRF is unity.

Where:

- SS_{Ax}, SS_{wtx} are standards peak areas and concentrations of surrogated standards added initially to the samples;
- IS_{Ax} and IS_{wtx} are the corresponding internal standards values as for the surrogate standards;
- RRF is the relative response factor of pure standards calculated from Equation 3.6 above, and;
- '*f*' represents the fraction of the initial, whole sample weight that is the analyte quantity prepared for hydrocarbon analysis.

The %Recovery values were used, in this study, as correction factors to calculate corrected component values for carboxylic acids, saturates and aromatic hydrocarbons only. On gas chromatogram of saturates, for instance, a 100% recovery is assumed when the surrogate standard, has a peak greater than that of the internal standard. Where % Recovery has been estimated, the calculated component amount, X_{wt} (Equation 3.4) was corrected using the relation:

$$X_{corr} = X_{wt} \times (\,100/\%Rec)$$

Equation 3.8 Expression for 'Corrected' analyte weight, X_{wt} value.

In general, RFs of components of interest relative to the standards were assumed to be unity (1.0). While this is not strictly true, it is sufficient for the purpose of sample comparisons in terms of compositional differences. Hence, data derived from this study, which are based on the said assumption, are semi-quantitative.

3.4.Simulated Migration Experiment

Figure 3.5 shows a general outline of the major stages of this part of the study. The samples used in the following experiments consisted of one light, mature, and apparently non-biodegraded North Sea crude oil (NSA03), and three size fractions of an immature

hydrocarbon-rich oil shale (Kimmeridge Blackstone) sample as the liquid (mobile) and solid (stationary) phases, respectively.

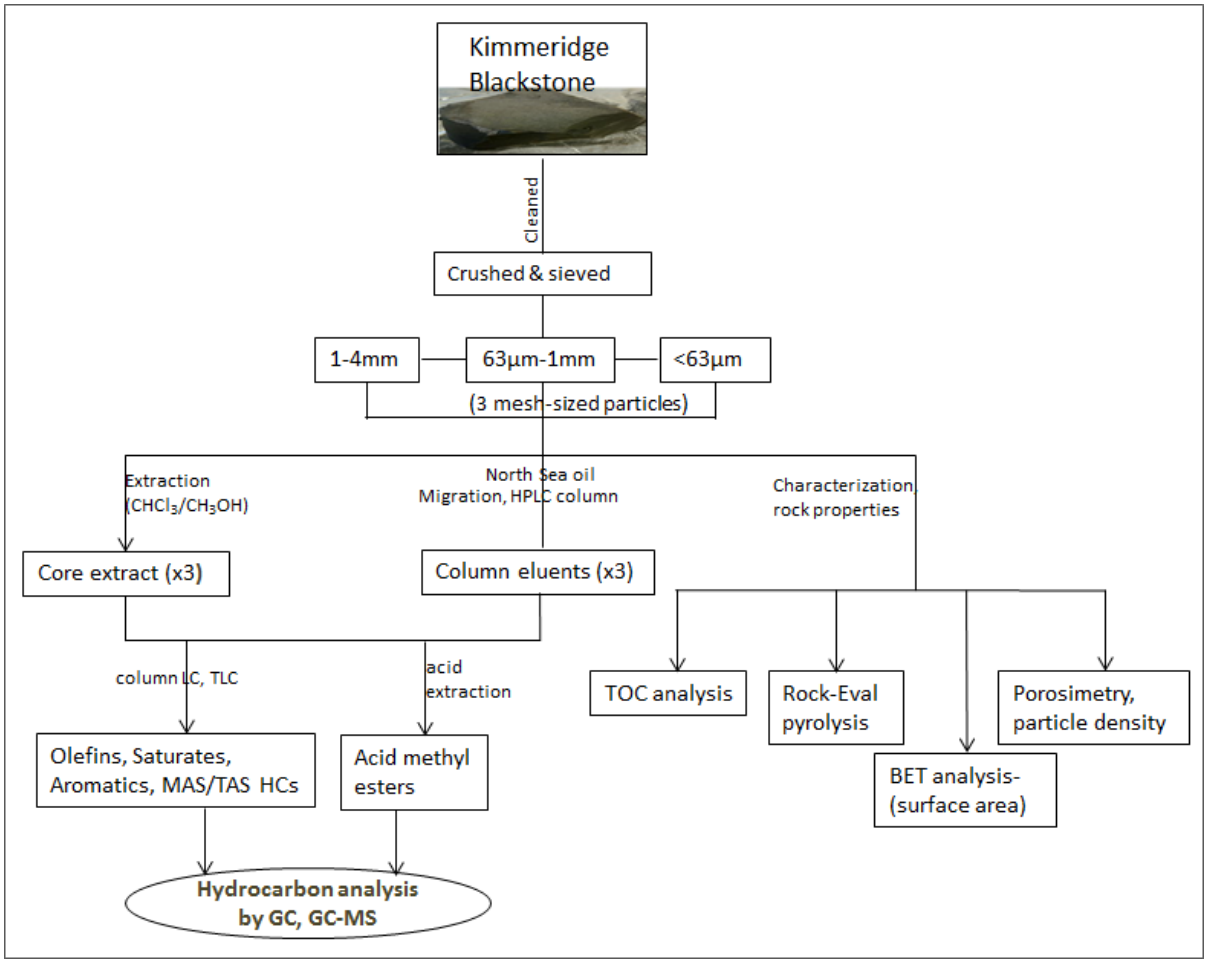


Figure 3.5 Overall procedures for the migration simulation experiment and the analysis of rock extract and collected oil fractions. Hydrocarbon composition of the North Sea oil was determined prior to the migration experiment.

The Kimmeridge Clay Formation (KCF) Blackstone sample, collected from the outcrop at Clavell's Hard, Kimmeridge Bay, Dorset, UK, was chosen as an example of an organic-rich immature rock from which mobile petroleum would potentially pick up other components. The composition (esp. olefinic) of the KCF Blackstone was determined by analysis of its solvent soluble, extractable organic matter (EOM).

3.4.1. *Kimmeridge Clay Sample Preparation*

The Kimmeridge Clay Formation (KCF) oil shale sample was noticeably a light weight dark grey coloured stone, with patches of weakly adhering whitish, weathered layers, and a visible embedded sea shell (point marked ‘x’ in Figure 3.6).

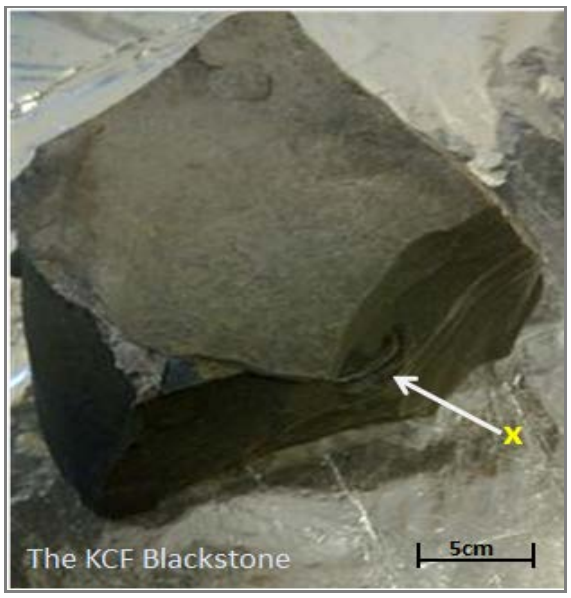


Figure 3.6 Photograph of the Kimmeridge Clay Formation black shale sample before sample preparations. Note the point marked 'x' is showing a visible shell fragment.

The rock surface was cleaned by first brushing with a steel brush to remove as much weathered layers from the rock as possible. This was then immersed in a large beaker containing DCM for 2-3 min to remove any external dirt or grease. It was removed, allowed to dry and kept in aluminium foil until it was processed further.

The rock was first reduced to smaller (<4 cm) pieces with a hammer and an aliquot of these were then ground in a rotary disc mill (Tema). Sieves for the three respective selected particle sizes (1-4 mm, 0.063-1 mm and <63 µm) were stacked in ascending size order onto a base plate into which the finest particles were collected; these were then used to size fractionate the crushed shale sample by manual shaking. About 100 g each of the three size fractions were obtained and placed in labelled glass jars ready for subsequent tests.

Different rock size fractions of the same mineral phase were selected in order to monitor the effects of varying grain sizes and thus surface areas in contact with the crude oil, on any fractionation effects on various oil components during the simulated oil migration. In particular, the experiments were designed to determine whether redistribution of marker compounds such as the olefins and acids could be accentuated when migration progresses through the finer particle sizes.

3.4.2. *KCF Soxhlet Solvent Extraction and EOM Analysis*

Aliquots (20-40 g) of the different particle size KCF rock samples were Soxhlet extracted for 24 hours using 400 ml of an azeotropic mix of DCM and methanol (93:7). Acid activated

copper turnings (~5 g) were added to the round-bottom solvent flask to remove any extracted elemental sulphur and as well as a few anti-bumping granules, and aliphatic and aromatic hydrocarbon surrogate standards as described previously. Aliquots of the extractable organic matter (EOM) obtained, were separated into hydrocarbon and acid fractions and analysed for selected compounds in them (as described previously for crude oil analyses).

3.5. Bulk Characterization of KCF Samples

Bulk characterization of the KCF Blackstone sample was carried out using a combination of physical and chemical analyses and performed in the CEG laboratories. These analyses included total organic carbon (TOC), Rock-Eval pyrolysis, surface area determination, mercury porosimetry, and particle density (Figure 3.5). Surface area analysis by BET was performed in the School of Chemical Engineering and Advanced Materials (CEAM) at Newcastle University.

3.5.1. *Total Organic Carbon (TOC) Analysis*

Total organic carbon (TOC) analysis was carried out on the prepared three particle sized samples to determine their TOC values (wt. %). An aliquot (ca. 100 mg) of the powdered rock sample was weighed accurately into a LECO porous silica crucible. These were then treated with 1-2 ml of warm (~50^{o}C) 4M hydrochloric acid solution to remove any carbonates from the samples. If required, additional acid was added until effervescence was no longer noticeable. After the acid had drained away, the sample was washed six times with 3 ml deionised water to remove the acid. The crucibles, with their decarbonated contents, were then dried overnight in an oven at 65-75^{o}C. Blanks were also run to account for any additional weight loss. Prior to sample analysis, the instrument was calibrated using a reference standard of known carbon content.

Determination of the (organic) carbon content was by combustion of the decarbonated samples in oxygen at 1200^{o}C using a LECO Model CS-244 carbon/sulphur analyser. The resultant CO_2 in the combustion gas was monitored using an infra-red detector (IRD) and quantified with reference to a LECO calibration standard (carbon and sulphur in steel) of known carbon content (ca. 0.8%) which was run after every 5 or 10 samples. The samples were analysed in duplicates and the instrument was recalibrated as needed to maintain results within the specified standard range. Results were reported as sample weight percent carbon.

3.5.2. *Source Rock Pyrolysis by Rock-Eval*

Rock Eval pyrolysis (Espitalié *et al.*, 1984, Espitalié *et al.*, 1985, Peters, 1986, Langford and Blanc-Valleron, 1990) was carried out on rock samples using a Delsi (Rock-Eval type) oil show analyser (OSA) fitted with Rock-plus software. A weighed aliquot (about 20 mg) of the powdered sample was placed in a crucible and heated under controlled temperature program in an inert gas pyrolysis oven. The program consisted of three stages of heating through which the pyrolysis progressed. Firstly, the sample was heated at 100^{o}C for a period of three minutes to enable the release of volatile gaseous hydrocarbons (S_0). The second stage is marked by an increase in the oven temperature to 300^{o}C; this was held isothermally for 3 min during which the free liquid hydrocarbons (oil) from the rock were volatilised giving rise to another peak, S_1. This was followed by a further and final ramping of the oven temperature from 300^{o}C to 550^{o}C at a rate of 25^{o}C/min and was held at the final temperature for two minutes. During this phase, the non-volatile organic matter (kerogen) in the sample was thermally cracked to generate more volatile compounds observed as the peak S_2. The temperature (T_{max}) at which the maximum of generated petroleum (S_2) occurred, was also recorded during the last phase. All volatilised hydrocarbons from the pyrolysis were detected and measured as peaks by a flame ionisation detector (FID). The total run time was approximately 15 min.

Ultimately, four basic parameters (S_0, S_1, S_2, and T_{max}) were directly measured from pyrolysis and are reported as milligram hydrocarbon/gram rock (mgHC/g). Two other important parameters: hydrogen index (HI = [S2/TOC] x 100) and production index (PI = $S_1/[S_1+S_2]$ were derived from a combination of the basic parameters.

3.5.3. *Surface Area Determination*

Since this technique is not commonly used in organic geochemical studies, this section introduces the basic concepts of determining the surface area of solid powders of organic compounds such as the grained sediment in this study. The surface area of sedimentary organic matter could be a crucial factor to understanding the mechanisms of uptake of non-source derived organic contaminants by crude oil during secondary migration (cf. de Jonge and Mittelmeijer-Hazeleger, 1996). Here the surface area of three different particle-sized fractions of a single immature highly organic-rich sample was measured using gas adsorption isotherms.

The gas adsorption method may be defined as the structural characterization of porous materials by the adsorption of condensed gas molecules, of known concentration, on unknown sample surfaces (Gregg and Sing, 1982, Rudzinski and Everett, 1991). The condensed gas quantities with their corresponding sample pressures are recorded and used in subsequent calculations. This data set measured at a constant temperature results in a constructed isotherm whose data is subject to series of calculation models to obtain surface area results. Principles of the BET, analysis procedures, measurement and data presentation are explained elsewhere in Appendix IV-f.

Application of the BET Method

The Brunauer-Emmett-Teller (BET) surface area is derived from a multilayer adsorption theory. The details of the theory is beyond the scope of this study but is based on the debatable assumption of an energetically homogenous surface. In other words, associated adsorbate-adsorbent energies at the first and subsequent layers of adsorbed molecules are identical (Gregg and Sing, 1982). The linearized BET equation, derived from the BET theory, is most often represented as:

$$\frac{\boldsymbol{p/p_o}}{\boldsymbol{n^a(1-p/p_o)}} = \frac{\boldsymbol{1}}{\boldsymbol{n_m C}} + \left(\frac{\boldsymbol{C-1}}{\boldsymbol{n_m C}}\right)\frac{\boldsymbol{p}}{\boldsymbol{p_o}}$$

Equation 3.9 The linearized BET equation.

Where:

- p = sample (residual) pressure;
- p_o = saturation vapour pressure at the measurement temperature;
- p/p_o = relative gas pressure (measurable within the range 0-0.995);
- n^a = the amount of gas adsorbed per mass of adsorbent at relative pressure p/p_o;
- n_m = monolayer adsorption capacity (volume);
- C = exponential constant related to the enthalpy (net heat) of adsorption

The unknown parameters 'C' and 'n_m' are determined from Equation 3.9 above. The isotherm data from experimental results is used to calculate the BET function, $(\frac{\boldsymbol{p/p_o}}{\boldsymbol{n^a(1-p/p_o)}})$ which is plotted against $(\frac{\boldsymbol{p}}{\boldsymbol{p_o}})$ to give a straight line plot (Figure 3.7). This plot is termed a *BET plot* and the range of linear relationship is restricted to a limited part of the isotherm within the range $0.05 \leq p/p_o \geq 0.30$ (Gregg and Sing, 1982, Lowell and Shields, 1991). The

value of the slope $\left(\frac{C-1}{n_m C}\right)$ and the Y-intercept $\left(\frac{1}{n_m C}\right)$ of the line are used to calculate the monolayer adsorbed gas quantity n_m and the BET constant C (Figure 3.7).

The next step in application of the BET method is calculation of the surface area from the BET function data, relative pressures, monolayer capacity (from the intercept on the Y-axis) and the BET constant (from the slope). In addition, the molecular cross-sectional area occupied by the adsorbate area, a_m, in the whole monolayer is required. Thus, the BET areas are given by the following expressions:

$$S_{total} = n_m . N_A . a_m$$

Equation 3.10 Total surface (BET) area.

$$S_{BET} = \frac{(S_{total})}{m_a}$$

Equation 3.11 Specific surface (BET) area.

Where: S_{total} and S_{BET} are the total and specific surface areas respectively; n_m is the volume of the adsorbate gas in units of volume/weight; N_a is Avogadro's number, a_m is the molecular cross-sectional area occupied by the adsorbing species in the complete monolayer; and m_a is the mass of the adsorbent sample.

Nitrogen is the most suitable and widely used adsorptive gas for surface area determination, thus for a close-packed BET monolayer, a_m (N_2) is assumed to be 0.162 nm^2 at 77K.

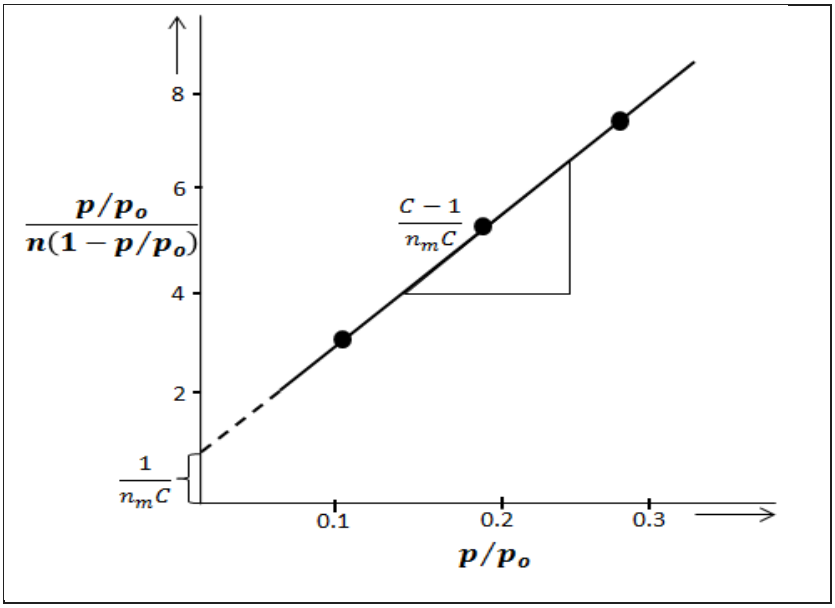


Figure 3.7 Typical BET plot (e.g. Brunauer *et al.*, 1938).

Limitations of result: Only the BET areas were derived in this work with no pairing data for comparisons. In addition, the accuracy and precision of the areas measured and recorded here are only the best approximation of the surface areas of these samples owing to the limited number of analyses and replicates and the overall condition of the instrument at the time of this study. The number of samples was also limited and this may hinder an attempt at correlation with other parameters.

3.5.4. *Mercury Injection Porosimetry*

Porosimetry is a term often used to include the measurement of all porosity-related attributes of a substance such as pore size, pore volume, density etc. The characteristics and physical behaviour of a material in its environment are mostly influenced by its porosity. Thus porosity is critical in understanding the origin, structure and possible use of many substances. The following sections briefly describe the theory and procedures for the mercury porosimetry analysis of the KCF rock sample for determining its pore volume and pore size distributions using a Micromeritics Autopore IV series, mercury injection column porosimeter. Basically, the sample was intruded with mercury at various pressures, and each pressure corresponds to a particular pore radius. The amount of mercury intruded was measured electrically at each pressure giving a measure of the pore size. This is known as mercury porosimetry or, more commonly, “mercury intrusion”. Porosity information finds many applications in petroleum exploration because it relates to the quantity and quality of petroleum that the bearing sediment can contain and hold, as well as how easily its components can be extracted (Dow, 1974).

As noted by Murray (1960) and Cook and Hover (1999), mercury does not wet most materials and surfaces and will not penetrate pores by free capillary action. Therefore, it must be forced to assume this action by applying an external pressure (Figure 3.8b). The amount of force required to intrude mercury through the pores of a substance varies inversely to the pore size of that material. The progressive intrusion of mercury into a porous structure under controlled pressures constitutes the mercury intrusion analysis. Here, pore volume and pore size distribution data are generated from the pressure and intrusion volume data using the Washburn’s equation. The accuracy of the resulting pore size data depends on the precision of the pressure measurements.

The determination of pore size following the technique of mercury intrusion is based on the unique combination of the non-wetting property and the high surface tension of mercury. A

liquid (mercury in this case) coming in contact with a solid porous material exhibits a non-wetting characteristic when the contact angle of the liquid with that solid material exceeds right angle. Consequently, the liquid cannot spontaneously penetrate the pores of the solid because its surface tension creates a force-resisting entry at the 'throat' (pore opening). The external pressure required to overcome this resistance depends on the pore size which is derived by series of equations (not detailed here) using the contact angle between the mercury and the material, as well as surface tension of mercury and perimeter of the pore opening (e.g. Washburn, 1921, De Gennes, 1985).

Therefore, for a cylindrical pore of radius, r, the absolute applied pressure, P, required to achieve pore intrusion is expressed by the force balance (Washburn's) equation as:

$$\boldsymbol{P = -\left(\frac{2\gamma cos\theta}{r}\right)}$$

Equation 3.12 The Washburn's equation.

Where: γ is surface tension of mercury (≈0.48 N/m at 20 °C under vacuum); θ is the contact angle of intrusion liquid (an average of 140° for mercury with most solids).

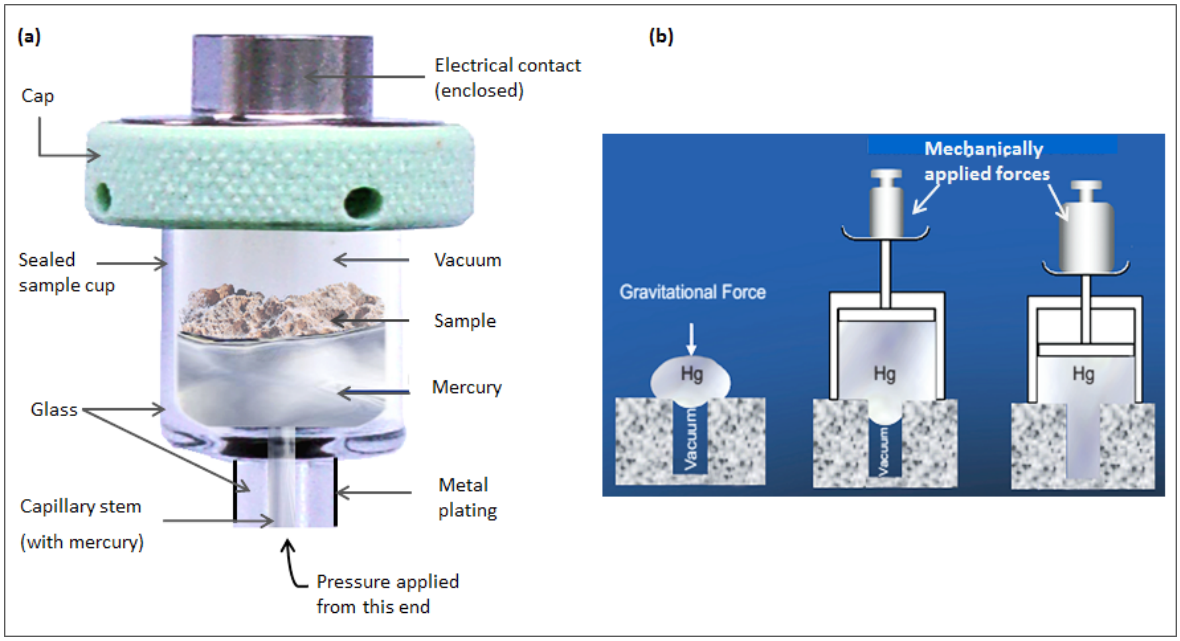


Figure 3.8 Diagram of (a) the main section of a mercury penetrometer showing mercury filling the sealed sample cup containing test sample; (b) An illustration of the principle of operation of the mercury penetrometer shown by a cross-section of a drop of mercury resting on a solid pore. Mercury must be forced into the pores of most substances by the application of external pressure due to its non-wetting property.

Procedures and Measurements

About 1g of the powdered sample was weighed and the 'clean' sample weight was determined after pre-treatment. The sample, held in a section of the penetrometer cell, was then pre-treated by evacuation to remove any adsorbed residual vapours from the pore system. This minimises artificial air pockets and contamination-related errors. Under reduced system pressure, the cell containing the sample was filled with mercury. A gradual increase of the overall pressure allowed the mercury to preferentially penetrate both sample pores and external void spaces. The larger pores were filled initially and then small and smaller pores were filled with increasing pressure.

The mercury penetrometer is an electrical capacitance dilatometer, constructed of an insulating glass and filled with a liquid conductor (mercury). The stem of the penetrometer is coated with a conductive metal and acts like a capillary-type reservoir for the analytical volume of mercury (Figure 3.8a). A separation of both conductors by an insulator (glass) forms a coaxial capacitor. As pressure forces mercury out of the capillary and into the sample, the mercury inside the capillary decreases and so is the capacitance. The decrease in capacitance, therefore, is proportional to the volume of mercury leaving the capillary with each change in pressure. This is the volume intruded into the pores and is monitored by the penetrometer device which is sensitive enough to detect a mercury volume change below 0.1 µl. By measuring the volume of mercury that intrudes into the sample material with each pressure change, the volume of pores in the corresponding size group is determined (Cook and Hover, 1999).

The first data reading was taken at 3 psi (pound per square inch) and then further incremental values were taken up to 39,000 psi. Corresponding pore sizes and volumes were directly obtained using the Washburn expression. The bulk density of the test sample was also calculated from the preliminary metric measurements but particle density was determined using simple pycnometry-type procedures and calculations are described in detail in later sections.

Limitations

The interpretation of mercury intrusion porosimetry data is based on assumptions of pore geometry and the interpretation of connectivity effects (De Gennes, 1985, Smith and Schentrup, 1987). Even the values for the contact angle and the surface tension cannot be

considered to be accurate but are rather “good assumptions”. Furthermore, the samples have to be dried prior to measurement and the degree of drying strongly influences the result. Another source of problems is created by artificial pores due to sample packing inside the penetrometer cell. Additionally, only relatively small samples can be analysed, which may not be a representative volume. A typical operating pressure range is between apparent pore entrance diameters of about 100 μm and 3.5 nm. The volume of mercury required to fill the smallest pore size can be limited by the maximum pressure achieved by the instrument while the largest measurable pore is limited by the height of the sample in the cell (Winslow and Diamond, 1970, De Gennes, 1985). Sample size is limited to dimensions of approximately 2.5 cm long by 1.5 cm wide. Mercury porosimetry does not measure the actual internal pore size but rather makes an estimate with the largest throat or pore opening from surface towards the pore. Nevertheless, mercury intrusion porosimetry is a powerful tool for a mostly qualitative analysis of the composition of mesoporous solids (Cook and Hover, 1999).

3.5.5. *Determination of Particle Density*

The particle density of the rock sample was determined using a Pycnometer (density bottle) Type 3 (Gay-Lussac), nominal volume 50 mL, with matched stopper. The pycnometer is a specially designed flask with a close-fitting ground glass stopper with a fine hole through it, so that a given volume can be accurately obtained. The rock was first crushed to pass through a 0.5 mm-0.1 mm sieve and oven-dried at 105°C. For control and reproducibility monitoring purposes, a portion of a quartz reference material with particle density 2.65 ± 0.02 g/mL was also analysed.

The pycnometer concept enables the density of pulverised solids to be measured accurately, by reference to an appropriate working fluid of known density such as water in which the powder is known to be completely insoluble (Flint and Flint, 2002) Using an analytical balance, weights were measured of the flask while empty, full of water, and containing the powdered sample whose density is being determined. The density of solid can be calculated using the weight of the sample obtained by difference, and the volume of displaced liquid after the pycnometer, containing the powdered solid, is filled with the test liquid. The weight of the displaced liquid and, consequently, the density of the solid particles can then be derived. Water was used as the testing fluid for the powdered sediment. It was de-aired prior to the analysis and all measurements were taken at 25°C. All preliminary measurements were performed and recorded as described in the following section.

Grain Density Procedures and Measurements

A clean, dry pycnometer (with the stopper removed) was weighed and the weight recorded (m_1) to the nearest 0.0001 g. Using a funnel, 2-3 g of the oven-dried sample was weighed and transferred to the pycnometer. The pycnometer plus sample, with the stopper removed, was weighed (m_2) and recorded to the nearest 0.0001 g. Sufficient de-aerated water was added to the pycnometer to just completely immerse the sample. The pycnometer was gently shaken to wet the sample thoroughly. The pycnometer contents and the beaker containing the de-aerated water were then placed in the vacuum desiccator and left under vacuum overnight. The pycnometer was then removed from the vacuum desiccator and carefully filled, to approximately two-thirds of the way up the neck, with de-aerated water. The pycnometer, without stopper, was placed in a water bath and the temperature of the water bath recorded (T_1). After a minimum of one hour, a second temperature reading (T_2) was recorded. The stopper was then carefully inserted into the pycnometer and removed from the water bath. The pycnometer, now containing the sample and water was dried and weighed. This weight (m_3) was recorded to the nearest 0.0001 g. The pycnometer was then emptied and thoroughly rinsed and filled to approximately two-thirds of the way up the neck, with de-aerated water. The previous steps, from placing the pycnometer in the water bath to drying and weighing it, were repeated. The weight of the pycnometer and water (m_4), to the nearest 0.0001 g, was measured and recorded.

Calculations

From the recorded weights and volumes from the above procedures, the particle density of the powdered KCF rock sample was calculated by the following expression:

$$\boldsymbol{\rho_s} = \frac{\boldsymbol{\rho_w(m_2 - m_1)}}{([\boldsymbol{m_4 - m_1}] - [\boldsymbol{m_3 - m_2}])}$$

Equation 3.13 Particle density of crushed KCF mudstone.

Where;

- ρ_s is the particle density of the soil in g/cm3;
- ρ_w is the density of water at the measured water bath temperature, g/cm3 (0.9970 at 25^{o}C);
- m_1 is the mass of the pycnometer, g;
- m_2 is the mass of the pycnometer plus dry soil, g;
- m_3 is the mass of the pycnometer plus dry soil plus water, g;

- m_4 is the mass of the pycnometer plus water, g.

The following precautions were taken while carrying out the above procedures in order to minimise experimental errors.

- A desiccator cage was placed over the vacuum desiccator whenever it was under vacuum.
- To prevent contamination of the glass surface of the pycnometer, which could introduce inaccuracies in weighing, handling of the pycnometer was kept to a minimum. Any handling of the pycnometer was done using tissue or lint free gloves.
- Each pycnometer and stopper was numbered. During the weighing, the pycnometer was matched with its corresponding stopper.
- It was ensured that the water level in the water bath was up to base of the neck of the pycnometer.
- When inserting the stopper, it was ensured that no air bubbles remained under the stopper by allowing it to sink under its own weight, so displacing the excess water. No rotary motion or undue pressure was applied after it has come to rest and was firmly seated. It was also ensured that the capillary tube in the stopper was completely filled with water.
- Great care was taken when drying the pycnometer, not to warm it by excessive handling, or to remove water from the capillary tube. Surplus water was removed from the top of the stopper by wiping once with the palm of the hand. The outside surface of the pycnometer was thoroughly dried using dry tissue without re-wiping the top of the stopper.
- Before it was reused, the pycnometer was rinsed several times to ensure complete removal of any residual solids.

3.5.6. *Migration Experiment Liquid Phase: North Sea Oil*

A non-biodegraded North Sea crude oil consisting of major hydrocarbon compounds was selected as the liquid phase for the artificial migration system. The oil is light with an API gravity of ~40, which gives it good solvent-like characteristics necessary for dissolving organic matter from surrounding sediments along its simulated migration pathway. However, the petroleum geochemistry of this oil indicated that it has not migrated through immature organic-rich sediments during its movement from source to reservoir, in its real migration system.

Prior to the migration study, initial hydrocarbon screening and carboxylic acid extraction and analysis were carried out on duplicate samples of the oil to determine its compositional makeup. These revealed a mature, seemingly non-biodegraded oil with, low abundance of carboxylic acids and very low amounts of unsaturated hydrocarbons (olefins), making it a suitable mobile phase for the migration experiments.

3.6.Simulated Migration System: HPLC Set-up

Some earlier studies in laboratory simulation of migration have introduced and developed methods to evaluate various compositional changes in oils caused by the effects of migration (e.g. Chakhmakhchev *et al.*, 1982, Bonilla and Engel, 1986, 1988, Brothers *et al.*, 1991, Krooss *et al.*, 1991, Trindade and Brassell, 1992). This study has adapted some of these methods to match its objectives as detailed in the following sections.

3.7. Procedures

A HPLC system comparable to that described by Bonilla and Engel (1986) as shown in Figure 3.9 was set up to simulate oil migration with the North Sea oil pumped through a solid phase of an organic-rich Kimmeridge oil shale contained within a semi-preparative HPLC column. The blank column system consisted mainly of a 25 cm x 10 mm I.D x 0.5″ O.D stainless steel HPLC column (Appendix I-c), liquid phase reservoir, controlled pressure/flow pump, and fraction collector (Figure 3.9).

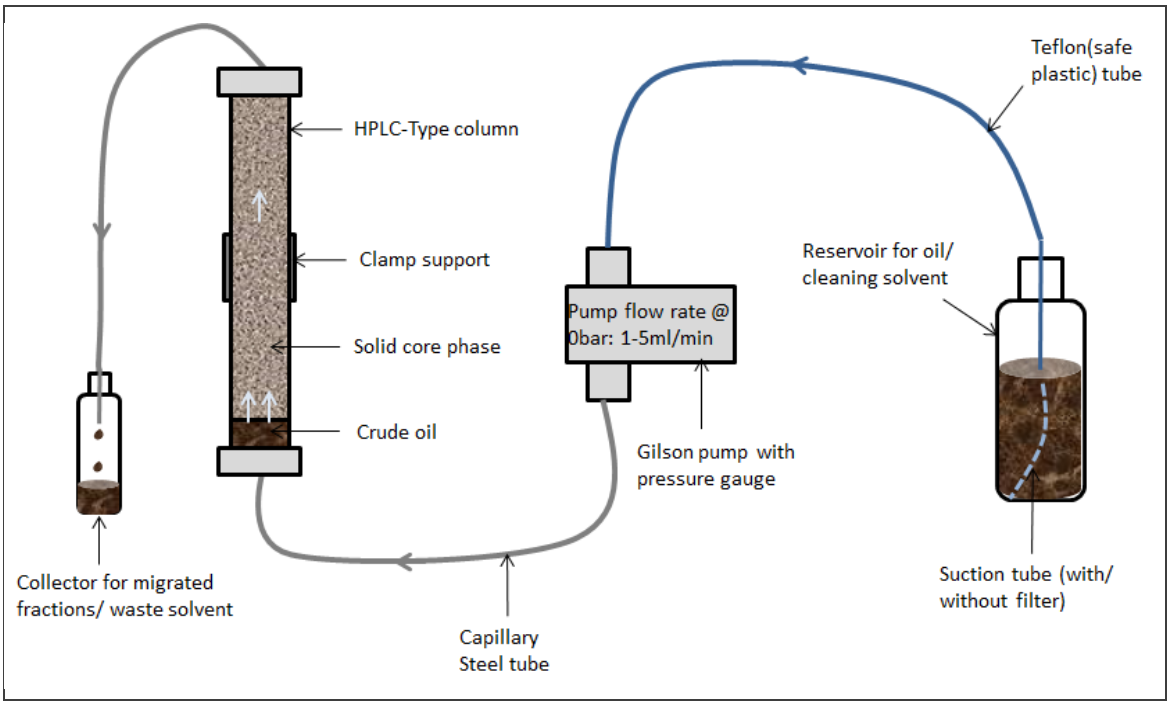


Figure 3.9 Schematic of the HPLC system set-up for the artificial migration experiments.

Initially the system was cleaned by flushing with hexane at 2 ml/min for 30 min from the solvent reservoir, through the tubes, column and into the collecting (waste) container. The column was detached from the set up and placed in the oven at ~60^{o}C to dry for half an hour.

The weight of the empty column assembly was first recorded. The dry column was then packed by hand with an accurately weighed portion of one of the three particle-sized rock fractions. The amount of sample required to pack each column varied inversely to its particle size. The reservoir was initially filled with about 800 ml of the 40^{o} API gravity crude oil. The lines were purged with the liquid sample (2 ml/min) to remove residual hexane from the system. The packed column was then reconnected to the system. All connections were physically monitored and checked for leakage. With the pump powered on, a gradual saturation of the system with the liquid (crude oil) phase was commenced until a flow rate of 100-200 µl/min was established at a steady pressure close to atmospheric. The column temperature was kept at room temperature (25^{o}C).

The void or dead (unoccupied) volume in the packed column as well as the length of time it would take for the column and sample to be fully saturated with the oil at any chosen flow rate were estimated using simple density-volume-mass calculations. Hence for any cylindrical steel column of given dimensions, the volume can be expressed as:

$$\boldsymbol{V_{col.} = \pi r^2 h}$$

Equation 3.14 Calculating the volume of the steel HPLC column.

Where: $\boldsymbol{r = I.D/2}$ (I.D is the internal diameter of the column given as 1 cm); h is the height or length of the column and given as 25 cm; substituting the values in Equation 3.14 gives the volume of the column as:

$$\boldsymbol{\pi r^2 h} = (\pi . 0.5^2 . 25) cm^3 = \boldsymbol{19.64\ cm^3}$$

Equation 3.15 Volume of the HPLC column.

Next, the volume of the sample in the column was estimated, given the bulk density from previous analyses, by the following expression:

$$\boldsymbol{V_s = \frac{W_s}{\rho_s}}$$

Equation 3.16 Volume of rock sample in the packed column.

Where: W_s is the measured weight of the sample and; ρ_s is the bulk density of the sample. Substituting in Equation 3.16, the volume occupied by the sample in the column was:

$$\therefore V_s \approx \frac{14.5g}{1.359gmL^{-1}} \approx \mathbf{10.67\ mL}$$

Equation 3.17 Calculated volume of sample in the column.

The void volume was then estimated as the difference, in volume, between the column, V_{col} and the sample, V_s calculated in Equation 3.15 and Equation 3.17 respectively. Thus:

$$\boldsymbol{V_{void} = (V_{col} - V_s)}$$

Equation 3.18 Expression for void volume in packed column.

$$\boldsymbol{V_{void}} = (19.64 - 10.67)mL = \mathbf{8.97\ mL}$$

Equation 3.19 Estimated column void volume.

The approximate length of time taken to completely saturate a packed column and its void volume by the oil phase at a given flow rate can be estimated. This is the time from which the first drop of eluent from the column is expected.

In the instance of charging the oil at 0.1 ml/min through a column of known volume (Equation 3.15), packed with given volume of sample (Equation 3.17), an approximation of the length of time was made based on the estimated void volume (Equation 3.19) and the flow rate only as:

$$\boldsymbol{t_{void} \approx \frac{V_{void}}{F_l}}$$

Equation 3.20 **S**aturation time of the packed sample prior to first oil elution.

Where: t_{void} is the approximate time taken to fill the volume, V_{void}, unoccupied by the solid phase, with the migrating liquid phase at a flow rate, F_l. From the above example,

$$\therefore\ T_{void} \approx \frac{8.97mL}{0.1mL/min} \approx 89.7mins$$

The first drops of column eluents were thus collected after approximately 1.5 hours.

These calculations were simplified, and did not consider other factors such as the dimensions of the lines through which the oil travelled before entering the system.

3.7.1. *Collection of Column (Migrated) Eluents and Column Extracts*

Aliquots of 2.5-5 ml of the column eluents were collected manually at hourly intervals in clean 10 ml glass vials labelled ‘a’-‘g’ and capped. The point of sample collection and the beginning and end of the migration system are depicted in Figure 3.10. The last vial ‘g’ was left to collect column eluents overnight at reduced flow rate of 50-100 µl/min for 15-17 hours.

Once the final eluent was collected and the oil flow was stopped, the volume of each eluted oil was measured. The column was detached from the LC system and weighed. The solid phase was then removed from the column; the crude oil held (with retained components) in the column, at the end of the system, was recovered by extracting the oil-soaked solid particles, three times for five minutes each time, with DCM. This was concentrated to minimum volume with a rotary evaporator at room temperature, and was further concentrated, but not completely dried, under gentle nitrogen gas stream, and weighed. All measurements are shown and discussed in the result chapter (5).

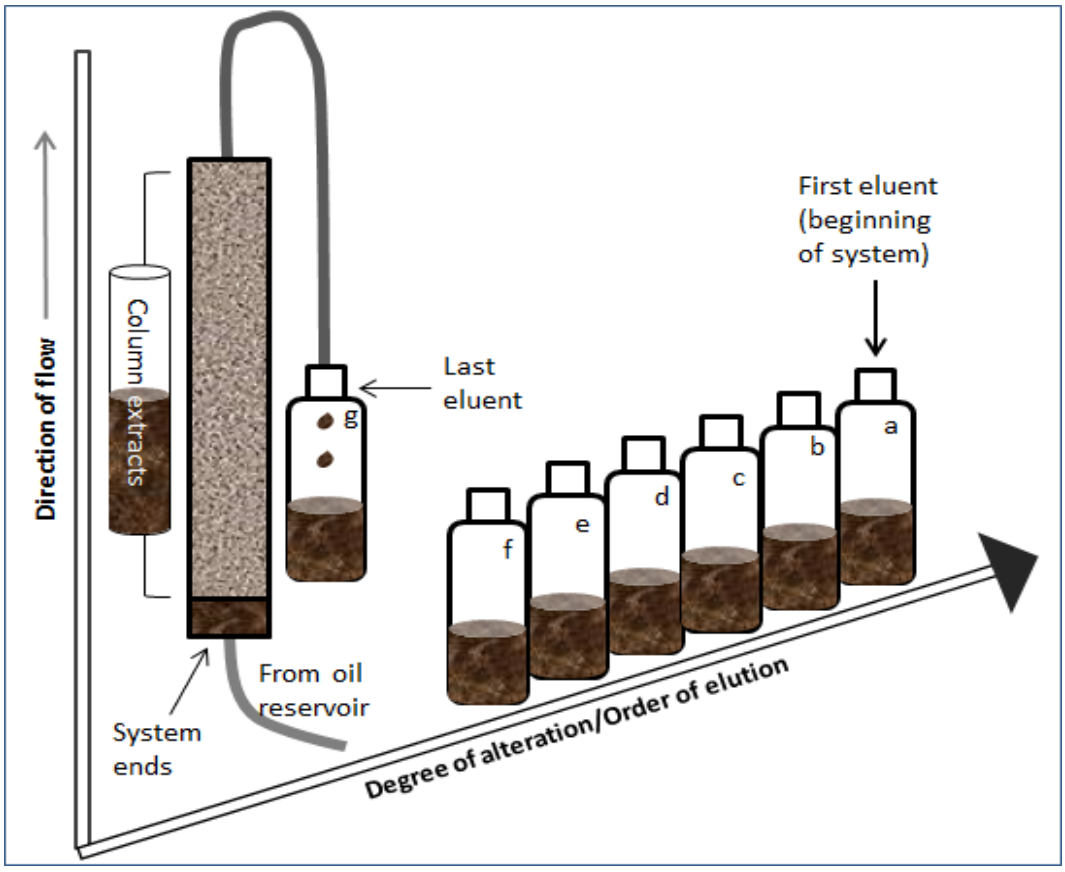


Figure 3.10 Illustration showing the flow path for the migration experiment. Migrated oils (a-g) were collected in the order in which they eluted off the steel column at time intervals (adapted from Brothers *et al.*, 1991).

These residual oil fractions will be referred to as ‘column extracts’ throughout the related Chapter 5. It is thought that the analyses of the column extracts could provide interesting

additional information about the behaviour of various petroleum components during migration especially with respect to their polarity differences within their common medium, and varying affinities to different mineral surfaces. In other words, although indigenous organic components within the migration column are expected to be dissolved in, and migrate with produced crude oil, these components, and those of the initial migrating oil could, in fact, be retained within the carrier bed rock matrix. This limiting factor to migration-contamination mechanism may be felt differently in both field and simulated migration settings, hence, the column extract is derived in an attempt to represent and/or measure such system differences, which could be useful in data interpretation and suggest ways of improving future migration studies.

As for the field (oil) samples, aliquots of all ‘migrated’ oil fractions, column extracts and KCF rock extracts were fractionated into saturated, unsaturated and aromatic hydrocarbons, and carboxylic acid fractions, and were all subject to similar procedures and analysis as previously described.

Chapter 4 Migration-Contamination Markers in Field Samples

4.0.Introduction

The occurrences of migration-contamination in certain crude oils are described in relation to the differences in abundance and distributions of the organic components that make up the oils and the source rocks from which they are thought to have been generated. This phenomenon has been proposed to be favoured in crude oils that have been generated and migrated under certain geological settings. Consequently, several published studies on migration-contamination and related migration alteration processes have recognised this process in reservoired oils from a number of settings, but especially in, Tertiary deltaic petroleum systems. However, these assumptions often do not take into consideration the molecular characteristics of the source rocks from which the supposedly altered oils were first expelled, due to the fact that many of the applicable source rocks were deeply buried and had not been sampled for characterisation. Hence inferences are drawn from assumptions from published data that the organofacies of these source rocks correspond to those of related oils in their initially generated stage; i.e. having not been significantly altered by migration or in-reservoir processes (Curiale, 2002).

Based on an extensive review of published literature and reviews on unusual biomarker distributions in some crude oils (Chapters 1 and 2), emphasis in this work is on olefins and acids as potential migration markers. Their occurrence and distributions in many of the relatively mature oils in the studied sample set form the basis of the work described in this section. The main objective of this chapter is to characterise crude oil samples from typical Tertiary deltas: Beaufort-Mackenzie, Kutei Basin and the Niger Delta. Routine molecular biomarkers and relatively rare organic compounds such as olefins and carboxylic acids are applied to assessing the incidence of migration-contamination occurring during secondary migration or accumulation, in these oils.

This chapter highlights the importance of some underutilised components of crude oil, and illustrate the potential for their application in routine geochemical studies especially biomarker analyses within prolific Tertiary deltas. Collating and interpreting these data should allow increased knowledge of, or what remains to be understood about the factors that control migration processes and their effects on the composition of petroleums in Tertiary deltaic basins.

4.1. Data Acquisition

The normal and isoprenoid alkane data were obtained from gas chromatography using the operating conditions described in the preceding chapter. Pentacyclic terpane and sterane data were generated from the m/z 191 and 217 mass chromatograms, respectively, by GC-MS as described in Chapter Three. Monoaromatic (MAS) and triaromatic steroid (TAS) hydrocarbon data were also derived from m/z 253 and 231 mass chromatograms respectively, by GC-MS. Data for other aromatic compounds were examined using their appropriate mass chromatograms via GC-MS analyses.

n-Alkene data were obtained from quantitated relevant peaks on m/z 55 mass chromatograms. Similarly, diasterenes and methyl-diasterenes were detected using m/z 257 and 271 mass chromatograms, respectively. Hop-17(21)-enes were monitored using m/z 367 mass chromatograms of the olefin fractions. In many of the Tertiary oils, a detectable but poorly resolved mix of oleanene isomers and urs-12-enes were quantified from m/z 204, 205 and 218 mass chromatograms. Sterenes were below detection limit in these samples. Tabulated lists of the full results of all analysed compounds are shown in Appendix III-a.

4.2. Characterisation by Conventional Molecular Marker Compounds

4.2.1. *Normal and Isoprenoid Alkanes*

The analysed Tertiary delta oils in this study are mostly non-biodegraded and they are characterised by normal alkane distribution from C_9 to C_{36}, usually peaking between *n*-C_{14} and *n*-C_{16}. Figure 4.1 shows typical saturated hydrocarbon fraction gas chromatograms for the Beaufort-Mackenzie, Kutei and Niger Delta oils.

While the majority of the case study samples are considered to be non-biodegraded as evidenced by their GC fingerprints (e.g. Figure 4.1 and Appendix III-c), it is important to note, particularly for the purpose of evaluating the origin of high concentration of carboxylic acids (discussed later in this chapter) in some of the tertiary deltaic oils, that some Beaufort-Mackenzie delta oils are heavily biodegraded. GC fingerprints of these oils (Appendix III-c), coupled with characteristic isoprenoid alkane ratios (Table 4.1), such as Ph/*n*-C_{18} (~1-20) indicated that BMD01, BMD02, CAN07 and CAN08 are severely biodegraded.

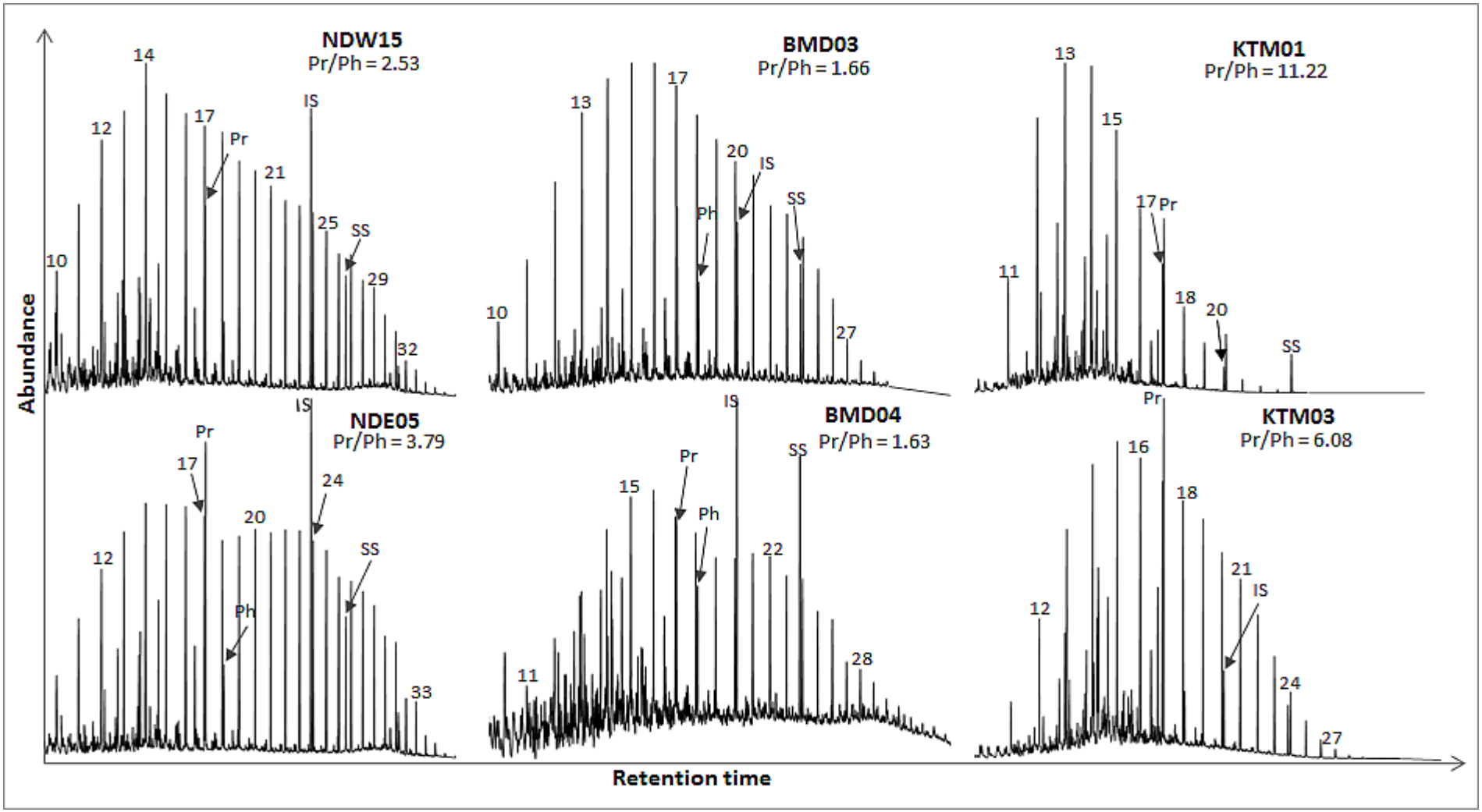


Figure 4.1 Gas chromatograms showing distributions of *n*-alkanes (~C_{10}-C_{36}) in representative crude oils from all three Tertiary deltaic basins. Sample codes: ND-, BM-, and KT signify oils from the Niger Delta, Beaufort-Mackenzie and the Kutei basins respectively. Carbon chain length is denoted by the digits shown; IS and SS are internal and surrogate standards respectively, and include n-heptadecylcyclohexane (<C_{24}), 5α-androstane (<C_{21}), and squalane (<C_{27}). Pr/Ph ratios were derived from the pristane and phytane peak areas.

These indicators also show that BMD04 is only slightly biodegraded, with pristane and phytane dominating most *n*-alkanes, and minimal loss of light end range molecules (Figure 4.1; Figure 4.2). For all eight samples studied from this region, the wax content is not distinctly apparent from the distributions. The pristane/phytane ratios are wide-ranging, from 0.36 to 5.08 (Table 4.1). There are only three Kutei oils in the sample set. These are mainly composed of $\leq C_{30}$ molecular weight compounds. Their *n*-alkane distributions, as shown in Figure 4.1 reveal that these oils are waxy, which is consistent with the physical properties of these oils. Typical gas chromatograms for two of the Kutei samples are shown depicting a unimodal distribution and depleted heavy-end alkanes. And, since the light-end molecules are generally intact in these samples, their characteristic molecular distribution corresponds to that of oils which have undergone migrational fractionation. Common *n*-alkane and isoprenoid alkane ratios are presented in Table 4.1. The pristane/phytane ratios for the Kutei oils range from 6.08 to 11.22. This is an indication that the depositional environment of the source rocks was predominantly oxic (e.g. Curiale *et al.*, 2005).

Table 4.1 Normal and isoprenoid alkane ratios from the study oils.

Sample ID	Pr/Ph	Pr/nC17	Ph/nC18	nC17/nC27	CPI-1	CPI-2	CPI-3
BMD01	0.36	0.83	1.04	26.47	1.57	2.37	2.01
BMD02	3.30	2.42	1.25	20.89	1.69	1.10	1.79
BMD03	1.66	0.63	0.43	5.19	0.83	1.04	0.94
BMD04	1.63	1.06	0.86	3.61	0.96	0.98	1.00
BMD05	1.09	0.63	0.70	143.21	0.90	1.16	0.98
CAN06	4.13	1.44	0.40	4.42	1.25	1.30	1.36
CAN07	5.08	4.35	10.68	44.15	n.d	0.60	n.d
CAN08	3.97	7.53	13.14	3.41	1.18	1.48	1.60
KTM01	11.22	1.42	0.21	n.d	n.d	3.84	n.d
KTM02	10.35	0.24	0.19	148.46	0.92	0.88	0.92
KTM03	6.08	1.12	0.24	21.34	0.93	1.15	1.07
NDE01	2.87	1.65	0.70	2.97	1.09	1.21	1.14
NDE02	2.78	1.51	0.58	1.68	1.17	1.14	1.15
NDE03	3.01	1.52	0.56	1.31	1.14	1.13	1.13
NDE04	2.69	1.27	0.54	1.74	1.14	1.12	1.12
NDE05	3.79	1.44	0.41	1.32	1.14	1.14	1.13
NDE06	2.71	1.37	0.57	1.62	1.13	1.14	1.12
NDE07	2.74	1.38	0.58	1.47	1.19	1.14	1.15
NDE08	4.29	1.18	0.33	2.40	1.16	1.19	1.19
NDW09	2.09	0.54	0.29	2.12	1.07	1.09	1.07
NDW10	1.91	0.40	0.24	1.84	1.07	1.09	1.07
NDW11	1.75	16.72	21.76	1.59	0.42	1.17	0.91
NDW12	2.71	0.48	0.20	2.01	1.08	1.10	1.10
NDW13	2.16	0.78	0.42	1.52	1.08	1.11	1.07
NDW14	1.77	2.53	1.69	1.78	1.33	1.12	1.23
NDW15	2.53	0.54	0.25	2.28	1.09	1.09	1.09
NDC16	3.20	1.00	0.35	5.87	1.08	1.12	1.11
NDC17	3.87	0.79	0.25	3.78	1.08	1.13	1.11
TRO01	1.59	0.46	0.33	2.36	0.98	1.03	1.00
NSA02	1.01	19.71	6.26	13.25	0.40	0.41	0.30
NSA03	1.35	0.53	0.48	4.28	0.99	1.03	1.01
NSA04	1.29	0.54	0.49	4.01	0.93	1.00	0.95
NSV05	1.53	0.76	0.62	4.30	0.93	0.99	0.96

Pr= pristane; Ph = phytane; nC17, nC18, nC27 are *n*-alkanes with 17, 18 and 27 carbon numbers respectively; CPI-1 ([2*C29]/[C28+C30]), CPI-2 (0.5*[(Sum-odd(C25-33)/(Sum-even(C24-32))+(Sum-odd(C25-33))/Sum-even(C26-34))], and CPI-3 ((C27+(6*C30)+C31)/((4*(C28+C30)) are the different derivatives of carbon preference index, also a measure of odd/even preference (OEP); nd = ratio was not derived due to non-detection or very low concentration of one or all compounds in the formula.

Seventeen oils from 3 different areas (North East, North West and Central shallow waters) of the Niger Delta (Table 3.1) were studied as part of the sample set. The representative alkane chromatograms, in Table 4.1, show that the Niger Delta crude oils are generally rich in both light and heavy end *n*-alkanes with a distribution range of C_9-C_{36} seen under the applied GC conditions (3.3.4). The waxiness of many of the Nigerian crude oils is evidenced by the relatively high abundance of *n*-alkanes greater than *n*-C_{22} in them. They exhibit a distinguishing attribute of non-biodegraded tertiary oils in their $\geq C_{32}$ extended range of normal alkanes (Volkman *et al.*, 1984). However, GC fingerprints and isoprenoid ratios (e.g. ph/*n*-C_{18}; Table 4.1) of a couple of samples from the western region (NDW11 and NDW14) of the delta, indicate moderate biodegradation. There is a unimodal distribution pattern for most oils with a few exceptions, as in the case of NDE05 (Figure 4.1), which may be suggestive of expulsion from source rocks deposited under either dysoxic or oxic conditions (e.g. Philp, 1994). The GC fingerprint enables a visual separation of the Niger Delta oils into those rich in low molecular weight ($\leq C_{21}$) *n*-alkanes and those rich in both low and high molecular weight *n*-alkanes. The pristane/phytane ratios for the Niger Delta oils range from 1.75 to 4.29 (Table 4.1), a reflection of variable source rock depositional conditions.

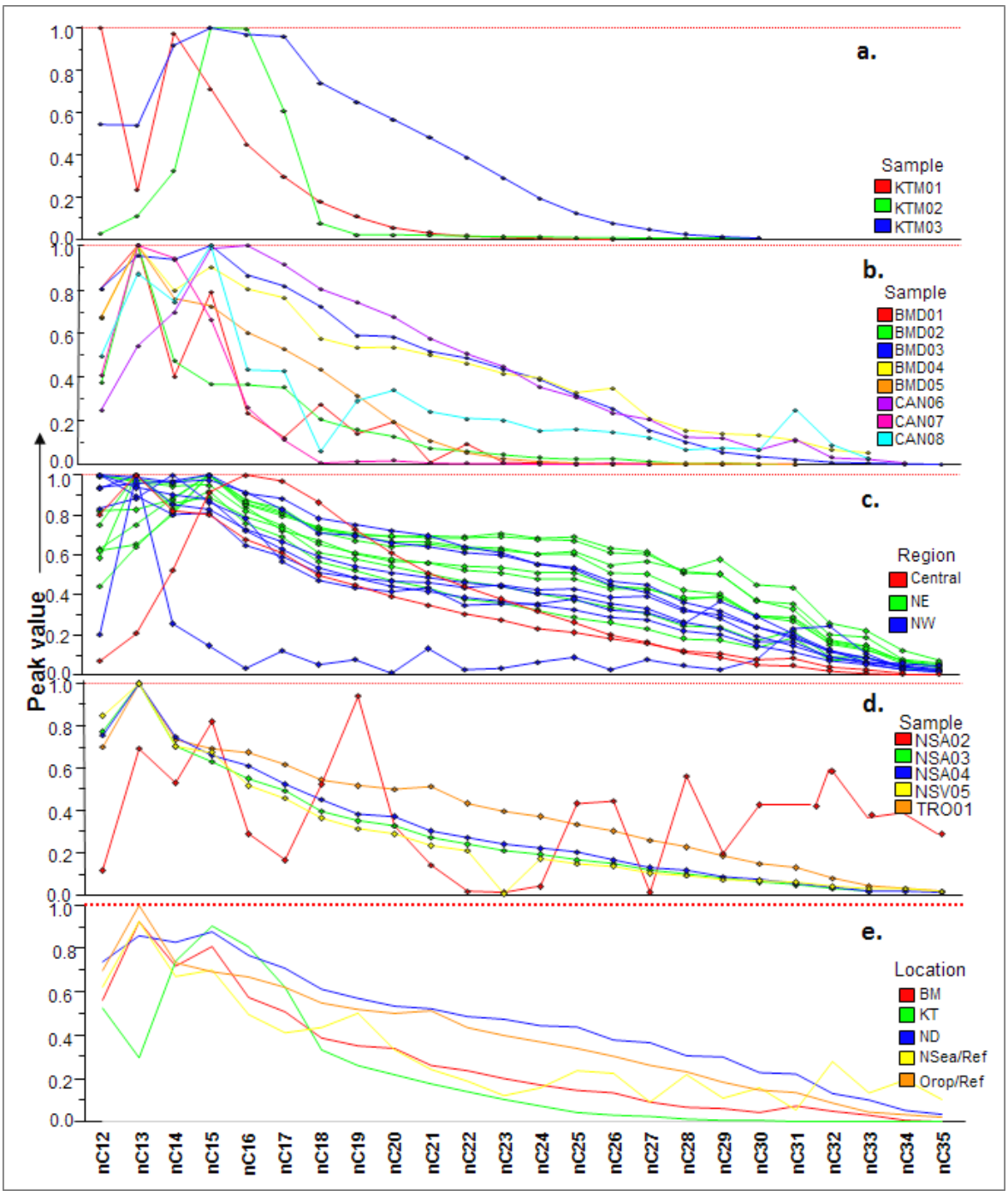


Figure 4.2 *n*-C_{12} to *n*-C_{35} *n*-alkane profiles for (a) Kutei- KT, (b) Beaufort-Mackenzie- BM, (c) Niger Delta- ND, and (d) the reference (NS's & TRO.) oils. Data were obtained from GC peak areas of *n*-alkanes, and normalised to the highest peak across samples within respective subsets. Bottom graph (e) shows reduced *n*-alkane distribution using data normalised to average values across sample groups.

The reference oil data are also included in the above table (Table 4.1) and their ratios are generally different from those of the case study oils, and are an indication that these oils are of predominantly anoxic marine source. However, two of these reference oils (TRO01 and NSA02) show some compositional differences from the rest of the reference samples, and resemblance with many of the case study oils. Derived parameters show that both oils are of mixed (marine/terrestrial) origin. The alkane distribution, in general, is a normal, unimodal

one in these Jurassic-type marine oils where there is mostly no carbon number preference as shown by the CPI values (Table 4.1). Besides the NSA02 being severely biodegraded (Ph/*n*-C_{18} > 6), the reference oils in this study are considered to be non-biodegraded (Appendix III-c; Table 4.1).

4.2.2. *Steranes and Diasteranes*

The sterane distributions are not consistent in the Beaufort-Mackenzie oils. The Canadian oils can be grouped into two families based on their C_{27}-C_{29} sterane distributions. While one group (e.g. BMD05, CAN06 and CAN07) contains high concentration of C_{29} steranes, the other oil group (BMD01, BMD02, BMD04 and CAN08) is characterised by low abundance of C_{29} relative, or in comparable proportions, to C_{27} and/or C_{28} steranes (Table 4.2). These characteristics generally reveal a predominantly terrigenous organic matter input to the source of the former group of oils while the latter group, also confirmed by lower C_{29}/C_{27} sterane ratios (<2; Table 4.2), is composed of oils that are sourced from marine or mixed (marine/terrestrial) organic matter type kerogen (Peters and Moldowan, 1993, 2005). This grouping is also depicted in a ternary plot (Figure 4.3) of C_{27}-C_{29} sterane and diasterane distributions in the Beaufort-Mackenzie Delta oils. All Beaufort-Mackenzie oils (except CAN06) are also rich in diasteranes, with a prevalence of the 13β(H),17α(H)-isomeric configuration and C_{29} abundance for most oils. The presence and distribution of C_{27}–C_{29} steranes and diasteranes in a typical sample (BMD04, Table 4.3) is shown in Figure 4.4. Identified peaks are denoted by ‘d’ and ‘S’ peaks for diasteranes and regular steranes respectively. As shown in the table of selected sterane and diasterane parameters and ratios (Table 4.2), the diasterane/sterane ratios for these oils range from 8.23 to 35.19.

Table 4.2 Sterane biomarker parameters and ratios derived for all crude oil samples.

Sample	%C27	%C28	%C29	ββC29	%C27dia	%C28dia	%C29dia	%DiaSt	Dia/Reg	St29S/R	St29I/R	C27ααS	C28ααS	C29ααS	Hop/St	StC29/C27
BMD01	34.96	17.09	47.95	0.42	14.64	20.00	65.36	8.23	0.39	0.93	0.73	0.17	0.22	0.48	1.09	1.37
BMD02	42.52	11.46	46.02	0.39	17.42	19.97	62.61	13.86	0.45	0.85	0.65	0.18	n.d	0.46	4.49	1.08
BMD03	n.d	n.d	n.d	1.00	29.56	39.21	31.23	66.45	1.00	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BMD04	28.66	33.85	37.49	0.51	27.22	41.14	31.64	35.19	0.57	1.22	1.04	0.54	0.54	0.55	0.44	1.31
BMD05	9.28	30.26	60.46	0.39	24.16	36.14	39.71	15.69	0.29	0.64	0.63	0.30	0.48	0.39	3.58	6.51
CAN06	30.47	17.62	51.91	0.33	19.43	32.40	48.17	15.14	0.31	0.63	0.50	0.20	0.46	0.39	6.91	1.70
CAN07	13.59	21.10	65.30	0.27	n.d	n.d	n.d	n.d	n.d	0.25	0.38	0.34	n.d	0.20	2.57	4.80
CAN08	30.90	21.93	47.18	0.40	23.62	37.16	39.22	15.04	0.27	0.75	0.68	0.20	0.42	0.43	4.32	1.53
KTM01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
KTM02	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
KTM03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
NDE01	30.23	26.12	43.65	0.39	22.59	32.06	45.35	16.31	0.32	0.86	0.63	0.43	0.52	0.46	30.36	1.44
NDE02	28.34	26.82	44.84	0.42	19.19	35.33	45.48	13.10	0.35	0.85	0.72	0.50	0.56	0.46	96.91	1.58
NDE03	27.57	26.94	45.49	0.40	23.48	29.31	47.21	14.82	0.36	0.99	0.65	0.50	0.52	0.50	69.02	1.65
NDE04	30.70	30.07	39.23	0.41	23.24	30.28	46.48	15.15	0.37	1.04	0.70	0.48	0.48	0.51	37.50	1.28
NDE05	26.82	24.01	49.16	0.38	20.25	30.68	49.07	13.45	0.38	1.05	0.61	0.50	0.51	0.51	192.27	1.83
NDE06	30.92	29.23	39.85	0.36	23.55	31.77	44.69	14.19	0.31	0.83	0.57	0.43	0.46	0.45	25.88	1.29
NDE07	30.69	28.97	40.34	0.38	22.05	31.29	46.66	13.42	0.32	0.83	0.62	0.43	0.47	0.45	28.39	1.31
NDE08	22.45	20.36	57.19	0.43	21.24	26.94	51.82	14.19	0.29	0.50	0.75	0.24	0.52	0.33	151.42	2.55
NDW09	33.16	27.88	38.96	0.39	25.97	33.01	41.02	18.05	0.33	1.02	0.64	0.44	0.45	0.50	54.69	1.18
NDW10	31.89	30.34	37.77	0.38	22.14	29.63	48.23	12.86	0.32	1.11	0.62	0.47	0.47	0.53	53.84	1.18
NDW11	32.35	31.75	35.89	0.43	24.21	29.28	46.51	11.65	0.28	1.43	0.75	0.42	0.45	0.59	29.28	1.11
NDW12	25.58	29.60	44.82	0.42	21.24	27.83	50.93	8.96	0.24	1.07	0.72	0.44	0.46	0.52	79.40	1.75
NDW13	31.40	26.37	42.23	0.35	22.19	32.68	45.13	13.07	0.32	1.05	0.55	0.43	0.45	0.51	52.94	1.34
NDW14	31.39	26.51	42.10	0.36	22.08	30.81	47.11	14.78	0.39	1.10	0.57	0.48	0.48	0.52	36.00	1.34
NDW15	26.65	27.35	46.00	0.36	21.69	28.85	49.46	14.55	0.37	0.91	0.57	0.47	0.51	0.48	87.59	1.73
NDC16	29.96	27.99	42.05	0.36	23.83	28.67	47.49	15.00	0.33	0.80	0.56	0.44	0.42	0.45	44.67	1.40
NDC17	30.14	34.37	35.49	0.44	21.09	32.88	46.03	11.04	0.30	1.12	0.78	0.42	0.42	0.53	69.17	1.18
TRO01	34.36	32.47	33.17	0.46	24.70	36.61	38.68	19.23	0.32	0.95	0.84	0.44	0.48	0.49	2.97	0.97
NSA02	32.12	30.92	36.96	0.54	29.77	28.79	41.44	31.57	0.63	1.80	1.17	0.54	0.59	0.64	1.72	1.15
NSA03	63.66	16.19	20.16	0.52	31.76	32.40	35.84	55.17	0.75	1.46	1.08	0.26	0.56	0.59	0.24	0.32
NSA04	67.66	16.79	15.55	0.56	34.94	33.78	31.28	54.66	0.71	1.87	1.27	0.24	0.54	0.65	0.33	0.23
NSV05	59.59	18.98	21.42	0.58	28.14	31.90	39.96	36.74	0.69	1.74	1.36	0.24	0.49	0.63	0.80	0.36

% C_{27}, C_{28} and C_{29} = C_{27}, C_{28}, C_{29} as % of sum C_{27}-C_{29} 5α(H),14α(H),17α(H)-20*R* sterane; ββ-C_{29} = 5α(H),14β(H),17β(H)-20*S*+R/5α(H),14β(H),17β(H)-20*R*+*S* + 5α(H),14α(H),17α(H)-20*S*+*R* C_{29} steranes; % C_{27}-, C_{28}- and C_{29}-Dia = % C_{27}- C_{29} in sum of C_{27}- C_{29} 13β(H),17α(H)-20*S*+*R* diasteranes; DiaSt is the % C_{27}-13β(H),17α(H) 20*S*+*R* diasteranes in total C_{29} 20*S*+*R* regular and isosteranes; Dia/Reg = Sum of C_{27}-13β(H), 17α(H) 20*S* and 20*R* diasteranes/ Sum of C_{27}-13β(H),17α(H) 20*S* and 20*R* diasteranes + sum C_{29}-5α(H),14α(H),17α(H)-20*S*+20*R* and 5a(H),14β(H),17β(H)-20*S*+20*R* steranes obtained from m/z 217 mass chromatograms; St29S/R is the ratio of 20*S* to 20*R* isomers of 5α(H),14α(H),17α(H)- C_{29} regular steranes; St29I/R is an index expressing Isosterane as a fraction of regular sterane for C_{29} by the sum of C_{29}-5α(H),14α(H),17α(H)-20*S*+20*R* and 5α(H),14β(H),17β(H)-20*S*+20*R* steranes; C_{27}-ααS, C_{28}-ααS and C_{29}-ααS (sterane isomerisation maturity parameter) = 20*S*/20*S*+20*R*- 5α(H),14α(H),17α(H) C_{27}, C_{28} and C_{29} regular steranes; Hop/St = 17α(H),21β(H)-hopane/ sum of all C_{27}-C_{29} regular and Iso-steranes; C_{29}/ C_{27} = ratio of C_{27}- C_{29} 5α(H),14α(H),17α(H)-20*R* sterane. n.d = not determined.

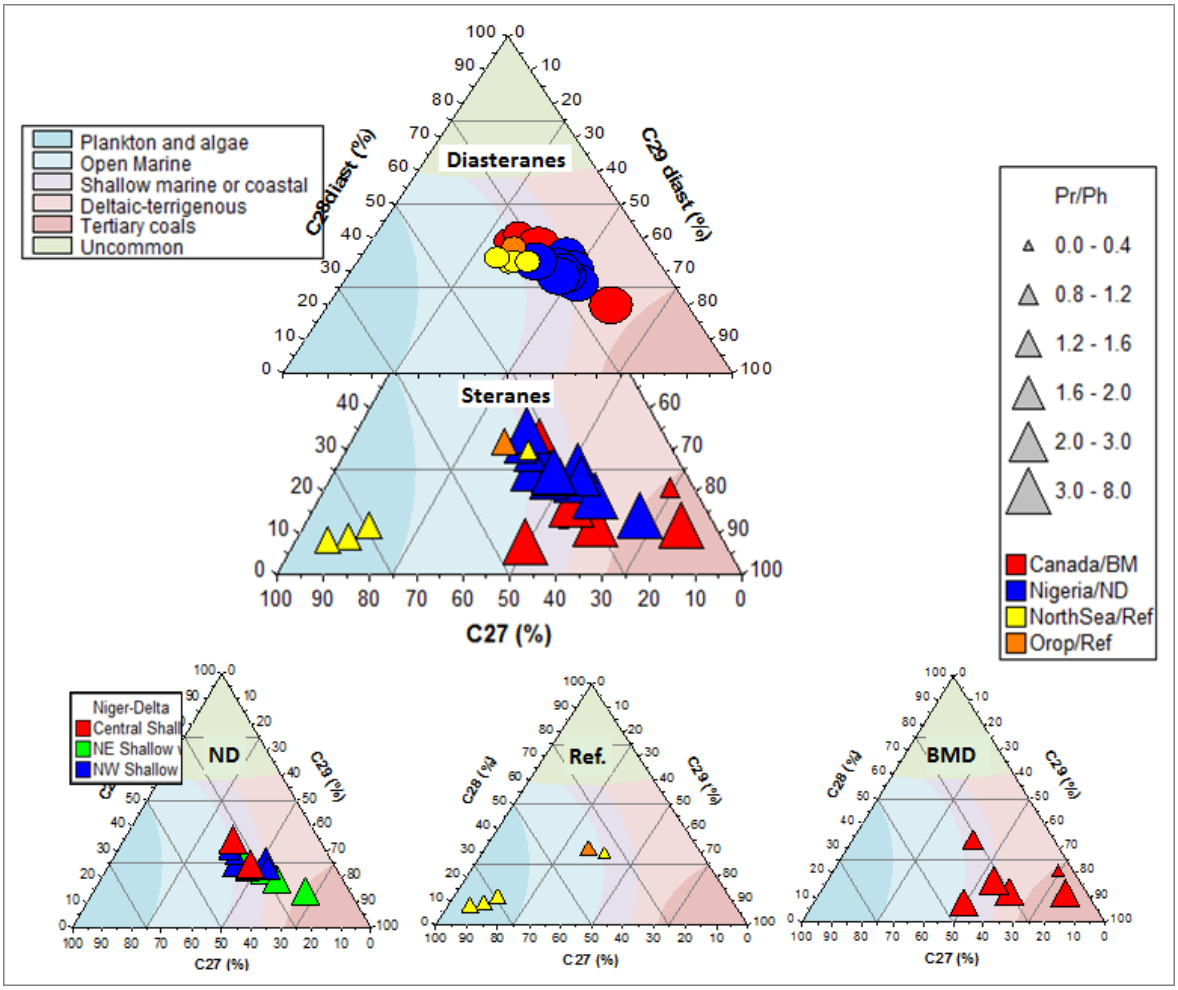


Figure 4.3 Ternary diagrams for steranes and diasteranes showing the distributions of ααα-20*R* isomers of cholestane (C_{27}), methylcholestane (C_{28}) and ethylcholestane (C_{29}) (bottom) and βα-(20*R* + 20*S*)-diacholestane (C_{27}), 24-methyldiacholestane (C_{28}) and 24-ethyldiacholestane (C_{29}) (top) respectively. Lower ternary plots show sterane distributions in individual sample subsets, Niger Delta (ND) and Beaufort-Mackenzie Delta (BMD). Plot was derived using pIGI geochemical analysis software. The various symbol (circle or triangle) sizes denote the range of Pr/Ph ratio in individual samples.

No sterane and diasterane biomarker parameters were determined for the three analysed Kutei condensate samples. This is due to the fact that these oils are mainly characterised by very low concentrations of biomarkers with higher abundances of low molecular ($\leq C_{27}$) weight compounds. Consequently, most sterane biomarkers are below detection limit. The Kutei samples thus could not be characterised by the ternary plot (Figure 4.3).

Table 4.3 Characteristic terpane source and maturity parameters for the study oils.

Sample	OL	Ts/Tm	BNH	30/29	NH/NM	Mor/Hop	Dia/NM	29(Ts/Tm)	32αβS	H-Hop	35/34	Gam-I	D30/H30	29Ts/30
BMD01	0.85	0.68	1.54	1.56	1.36	0.49	1.47	1.52	0.51	0.59	1.01	0.17	0.69	0.97
BMD02	0.24	0.45	n.d	1.57	2.91	0.19	0.67	0.32	0.56	0.49	0.47	0.04	0.15	0.20
BMD03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
BMD04	0.12	1.26	0.17	2.30	4.53	0.16	2.02	0.49	0.58	1.20	1.05	0.10	0.19	0.22
BMD05	0.40	0.69	n.d	2.00	2.48	0.20	0.58	0.61	0.58	0.53	n.d	0.05	0.12	0.30
CAN06	0.31	0.70	n.d	1.90	4.00	0.20	0.88	0.47	0.57	0.47	0.50	0.03	0.12	0.25
CAN07	0.55	0.60	n.d	2.68	0.64	0.27	0.00	1.36	0.61	0.35	n.d	0.14	n.d	0.51
CAN08	0.30	0.67	n.d	1.95	4.05	0.22	0.88	0.32	0.57	0.51	0.62	0.03	0.11	0.16
KTM01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
KTM02	0.83	n.d	n.d	1.57	n.d	n.m	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
KTM03	0.81	0.72	n.d	0.82	n.d	n.m	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
NDE01	1.33	0.66	0.12	1.37	6.36	0.19	0.45	0.29	0.58	0.43	0.35	0.04	0.05	0.21
NDE02	1.60	0.68	0.17	1.40	6.05	0.20	0.71	0.20	0.57	0.41	0.60	0.03	0.08	0.15
NDE03	1.88	0.74	0.20	1.14	5.81	0.24	0.75	0.32	0.58	0.44	0.55	0.04	0.11	0.28
NDE04	1.19	0.73	0.12	1.37	5.92	0.20	0.65	0.31	0.58	0.46	0.45	0.03	0.08	0.23
NDE05	1.74	0.71	0.26	1.33	7.13	0.20	0.80	0.21	0.58	0.36	0.82	0.02	0.08	0.16
NDE06	1.16	0.61	0.12	1.26	4.87	0.20	0.50	0.26	0.56	0.47	0.51	0.03	0.08	0.21
NDE07	1.53	0.77	0.16	1.22	4.88	0.23	0.62	0.30	0.56	0.48	0.56	0.04	0.10	0.25
NDE08	2.05	0.63	0.24	1.26	7.57	0.21	1.12	0.31	0.56	0.28	0.00	0.01	0.12	0.25
NDW09	0.50	1.17	n.d	1.65	5.32	0.15	0.58	0.31	0.58	0.53	0.60	0.05	0.07	0.19
NDW10	0.42	0.99	0.05	1.70	5.10	0.18	0.69	0.30	0.56	0.61	0.55	0.05	0.08	0.18
NDW11	0.45	1.10	0.07	1.49	5.82	0.17	0.62	0.30	0.58	0.56	0.65	0.07	0.07	0.20
NDW12	1.23	0.81	0.22	1.18	5.42	0.21	0.74	0.29	0.56	0.36	0.51	0.02	0.12	0.24
NDW13	0.71	0.93	n.d	1.30	4.03	0.21	0.61	0.32	0.58	0.51	0.68	0.07	0.12	0.25
NDW14	0.72	0.90	n.d	1.31	4.02	0.23	0.72	0.40	0.57	0.54	0.72	0.11	0.14	0.31
NDW15	1.54	1.04	0.17	1.19	5.15	0.21	0.70	0.29	0.56	0.38	0.54	0.05	0.11	0.25
NDC16	1.01	0.83	0.09	1.33	5.69	0.18	0.65	0.24	0.56	0.31	0.37	0.03	0.09	0.18
NDC17	0.98	0.70	0.09	1.31	6.44	0.19	0.77	0.27	0.56	0.29	0.46	0.02	0.09	0.20
TRO01	0.17	0.83	0.21	1.64	4.82	0.20	1.13	0.33	0.58	0.66	0.89	0.16	0.14	0.20
NSA02	0.11	1.36	0.29	1.63	5.12	0.20	1.90	0.52	0.59	1.60	1.14	0.09	0.23	0.32
NSA03	0.06	2.37	0.04	2.65	15.56	0.16	12.09	0.87	0.56	1.84	0.92	0.08	0.29	0.33
NSA04	n.d	2.27	0.03	2.49	n.d	0.17	n.d	0.79	0.59	1.65	0.99	0.08	0.25	0.31
NSV05	n.d	1.72	n.d	2.28	6.66	0.13	2.72	0.46	0.60	1.15	0.86	0.05	0.18	0.20

OL = 18α(H)-+18β(H)-oleanane/17α(H), 21β(H)-hopane; Ts/Tm = 18α(H)-22,29,30-Trisnorneohopane (C_{27}Ts)/17α(H)-22,29,30-trisnorhopane (C_{27}Tm); BNH (Bisnorhopane index) = 17α(H)-28,30-bisnor-C_{28}Hopane/17α(H), 21β(H)-C_{30}-hopane; 30/29 = 17α(H), 21β(H)-C_{30}-hopane/17α(H),21β(H) 30-nor-C_{29}-Hopane; NH/NM is the ratio of 17α(H), 21β(H)-30-nor-C_{29}-Hopane to 17β(H), 21α(H)-30-nor-C_{29}-Moretane; Hop/Mor = I7α(H), 21β(H)-hopane/17β(H), 2Iα(H) hopane (moretane); Dia/NM = 17α(H)-Diahopane-C_{30}/17β(H), 21α(H)-30-nor-C_{29}-Moretane; 29(Ts/Tm) = 18α(H)-30-norneohopane (C_{29}Ts)/17α(H), 21β(H)-30-norHopane; 32αβ*S* = 17α(H), 21β(H)-bishomohopane 22*S*/ 22*S*+22*R*; H-Hop is the sum of all 17α(H), 21β(H)-22*S*+22*R* for C_{31}-C_{35} hopanes relative to the sum of 17α(H) 22,29,30-trisnor-Hopane(C_{27}Tm), 17α(H),21β(H) 30-nor- C_{29}Hopane and 17α(H),21β(H) C_{30}-Hopanes; Hop(35/34) = ratio of 17α(H), 21β(H)-pentakishomohopane (22*S*+22*R*) to 17α(H), 21β(H)-tetrakishomohopane (22*S* +22*R*). Gam-I (gammacerane index) is the ratio of gammacerane to C_{30}-17α(H), 21β(H)-hopane; D30/H30 = 17α(H)-Diahopane/17α(H), 21β (H)-hopane; 29Ts/30 is 18α(H)-30-norneohopane (C_{29}Ts) relative to 17α(H), 21β(H)-C_{30}-hopane. 'n.d' or zero values means the parameter could not be derived due to the absence of one or all of the components in the formula.

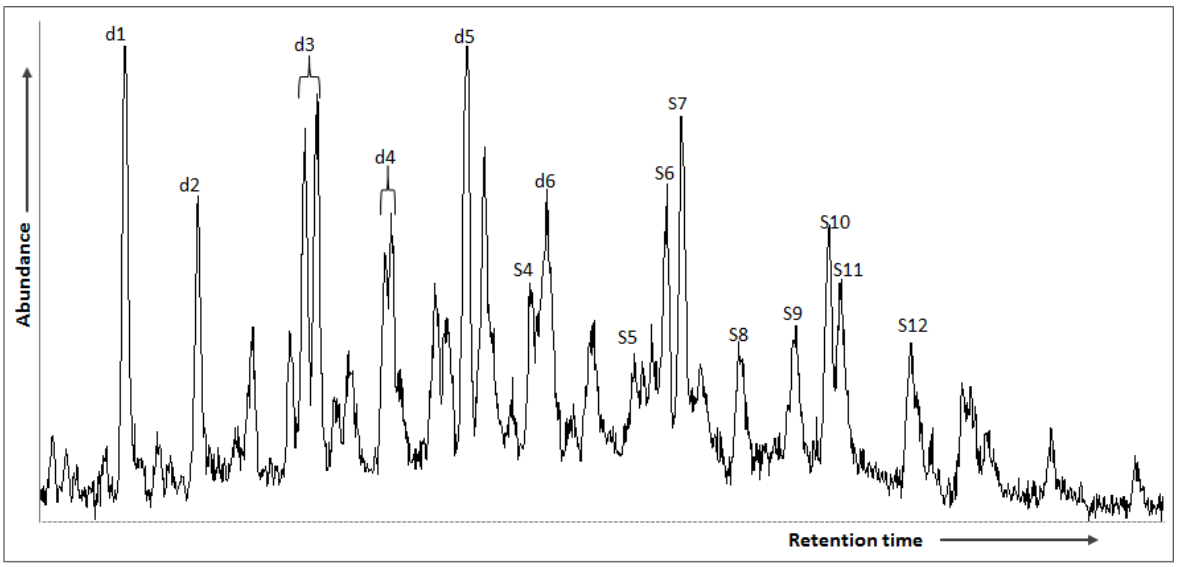


Figure 4.4 Representative partial m/z 217 mass chromatogram showing the sterane and diasterane distribution in a Beaufort-Mackenzie Delta oil (BMD04). The 'd' and 'S' symbols represent the diasterane and sterane peaks respectively. Full peak identification is given in Appendix II-a.

The Niger Delta oil set shows a generally similar sterane distribution (high % C_{29} relative to %C_{27} and C_{28} steranes; e.g. Figure 4.5; Table 4.2) that is characteristic of terrigenous organic matter input (e.g. Seifert and Moldowan, 1978, Peters and Moldowan, 1993). A fairly consistent distribution of C_{27}-C_{29} steranes (22-32%C_{27}, 24-34%C_{28}, 35-57%C_{29}) and diasteranes (19-26 %C_{27}, 27-35 %C_{28}, 45-52 %C_{29}) was observed for most oils in this sample subset (Table 4.2). This could be an indication of common source material for these oils, most of which are mature and non-biodegraded. The diasteranes are generally more abundant and exhibit more consistent distributions than the steranes (Table 4.2), probably due to their higher thermal stability (Peters and Moldowan, 1993) and further resistance to biodegradation (e.g. Philp and Gilbert, 1982). The observed C_{29}/C_{27}- sterane ratios for the Niger Delta oils ranges from 1.11 to 2.55. These observations reflect oils expelled from source rocks that received varying proportions of marine and more terrigenous organofacies deposited within both oxic (deltaic) and less oxic (shallow/open marine) conditions (e.g. Table 4.2, Eneogwe and Ekundayo (2003). In general, based on the Hop/St ratio, the Beaufort-Mackenzie Delta oils are distinguished from their Niger Delta counterpart by their obviously lower ranging values for these ratios (1.09-6.91 versus 25.88-192.27, respectively).

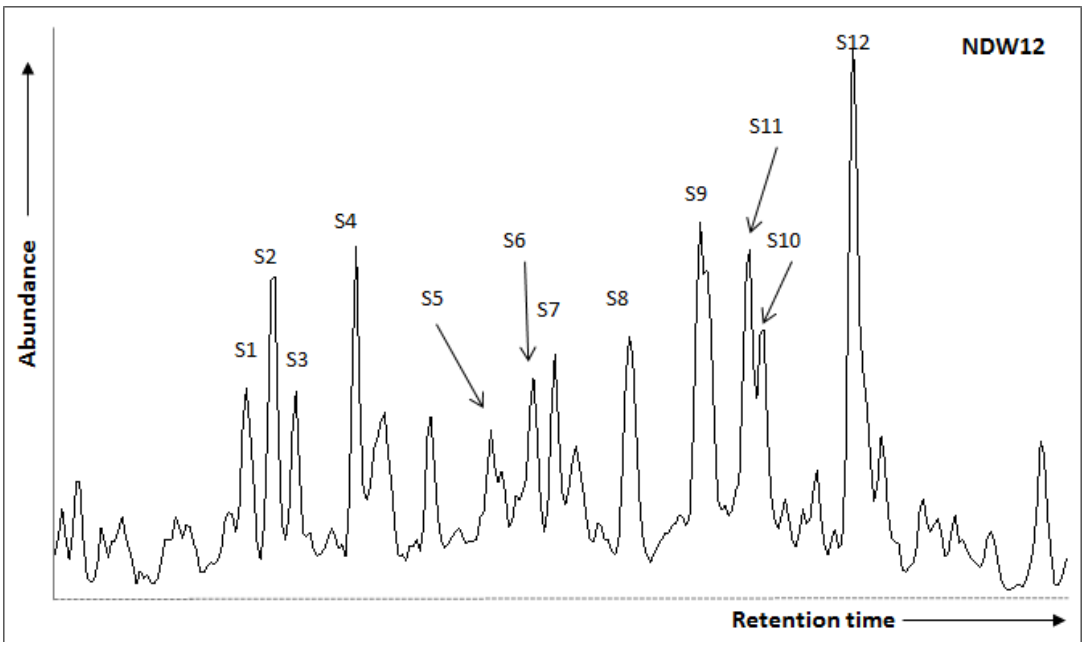


Figure 4.5 Representative partial m/z 217 mass chromatogram showing the sterane distribution in a Niger Delta oil (NDW12). The symbol 'S' denotes sterane peaks. Full peak identification is given in Appendix II-a.

The reference oils are again markedly distinguished as marine oils by their higher $\%C_{27}$, lower StC_{29}/C_{27}, and very low Hop/St ratios. Maturity parameters, such as St29S/R (Table 4.2), also revealed that these oils are generally more mature than the case study Tertiary deltaic oils. TRO01 and NSA02 are also seen to be distinct in this oil set by many of the parameters shown in the above table, with some characteristics (e.g. StC_{29}/C_{27}, $\%C_{29}$dia, $\%C_{28}$ and Hop/St) of terrestrially sourced oils, and comparable to most of the case study samples (Table 4.2).

4.2.3. *Triterpanes*

Although detailed examination of *m/z* 191 mass chromatograms of typical oils (Figure 4.6) show several other unidentified compounds, hopanes and moretanes are seen to be widespread in the study oils. They cover the C_{27}-C_{35} carbon number range in most samples and are seen to dominate the entire triterpane distribution. However, some other compounds such as oleananes and gammacerane, though not ubiquitous like the hopanes, were also identified. The distributions of such compounds in oils are useful for predicting thermal maturity, organic matter source and geological age (e.g. Ekweozor and Telnaes, 1990, Curiale, 1991, Sinninghe Damsté *et al.*, 1995).

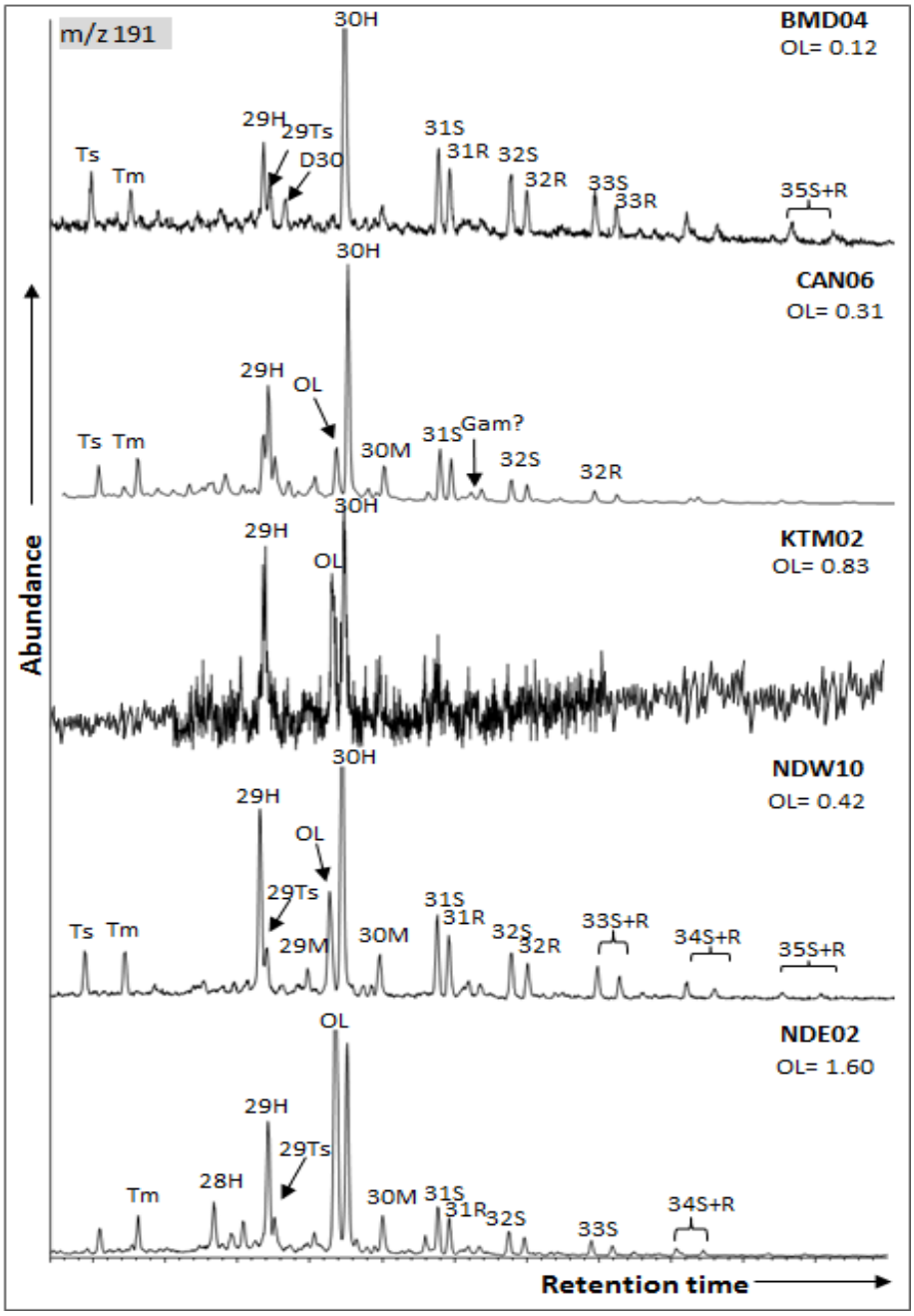


Figure 4.6 Partial m/z 191 mass chromatogram showing distribution of major triterpanes, up to C_{35} compounds, in selected crude oils of the Beaufort-Mackenzie (BMD04, CAN06) Kutei Basin (KTM02), and the Niger Delta (NDW10, ND02); BMD04 and NDE02 show characteristics of a typical marine (mixed with some terrestrial plant input), and a terrigenous oil respectively. KTM02 is biomarker-deficient as depicted. Gammacerane is tentatively identified, but are relatively low in most samples. Full peak identities are shown in Appendix II-b.

The grouping of Beaufort-Mackenzie oils based on the triterpane distributions corresponds with those of the sterane distributions. The oleanane parameter varies widely for these samples, and oils with low oleanane concentrations relative to C_{30}-αβ-hopanes are thought to have received relatively low higher plant contribution to their source OM, while those with high oleanane index have high land plant (angiosperm) organic matter input (Czochanska *et al.*, 1988, Ekweozor and Telnaes, 1990, Nytoft *et al.*, 2002). In most cases, these conclusions are also evidenced by other terrigenous triterpane indices, such as Ts/Tm

and D30/H30 (Table 4.3). Diahopane, though present in coals and terrigenous sourced oils (Philp and Gilbert, 1986), is a not a specific terrigenous marker as high diahopane content in oils can also be due to high thermal maturity. They are also believed to be considerably present in marine-sourced oils due to existence of a combination of lithological and depositional factors (clay and oxicity) that controls the diahopane/hopane ratios in oils within the marine environment. The oleanane indices for the Beaufort-Mackenzie oils range from 0.12 to 0.85, indicating variable oil maturities or level of terrigenous higher plant input to source deposition (Snowdon and Powell, 1979, Brooks, 1986b, Curiale, 1991). Figure 4.6 shows representative m/z 191 mass chromatograms including those for typical oils (BMD04, CAN06) in this sample subset. Many of the oils of Kutei Basin have low biomarker concentrations and significant peaks could neither be resolved, integrated or quantified. Consequently, many of the terpane ratios and parameters were not derived for this sample sub-set.

Also consistent with the grouping based on the sterane distribution, and as previously described for the Beaufort-Mackenzie oils, the pentacyclic triterpanes can be used to classify the Niger Delta oils into two oil types. They include those with relatively high oleanane (oleanane index); and a second group exhibiting a significantly lower oleanane index. Figure 4.6 shows typical m/z 191 chromatograms reflecting this oleanane-based characterisation in representative Niger Delta oils: NDW10 is a crude oil from the western section of the delta having low oleanane content; and the eastern section NDE02, with comparatively high oleanane abundance. Most oils, however, fall in between these extreme groups.

Gammacerane was detected in most samples and its relative abundance (also measured as the Gammacerane index) is low (0.01-0.11) or not measurable (Table 4.3). Calculated terpane source and maturity biomarker parameters for the Niger Delta oil set are shown in Table 4.3. The high hopane/sterane ratios exhibited by a majority of the oils is a reflection of abundant land plant-related bacterial input. The abundance of gammacerane compares inversely with the Pr/Ph ratios and oleanane indices for most oils. The oils of the Niger Delta sections (North-East, North-West and Central shallow waters) are systematically grouped by the gammacerane index vs. pristane/phytane ratio relationship (Figure 4.7) in terms of their depositional environment and organic matter source. The ellipses on the graph (Figure 4.7) are used to correlate and classify the samples sets and subsets based on their source rock depositional environment and lithology with reference to the ‘reference’ oil sample set, which have been established to be of predominantly marine source.

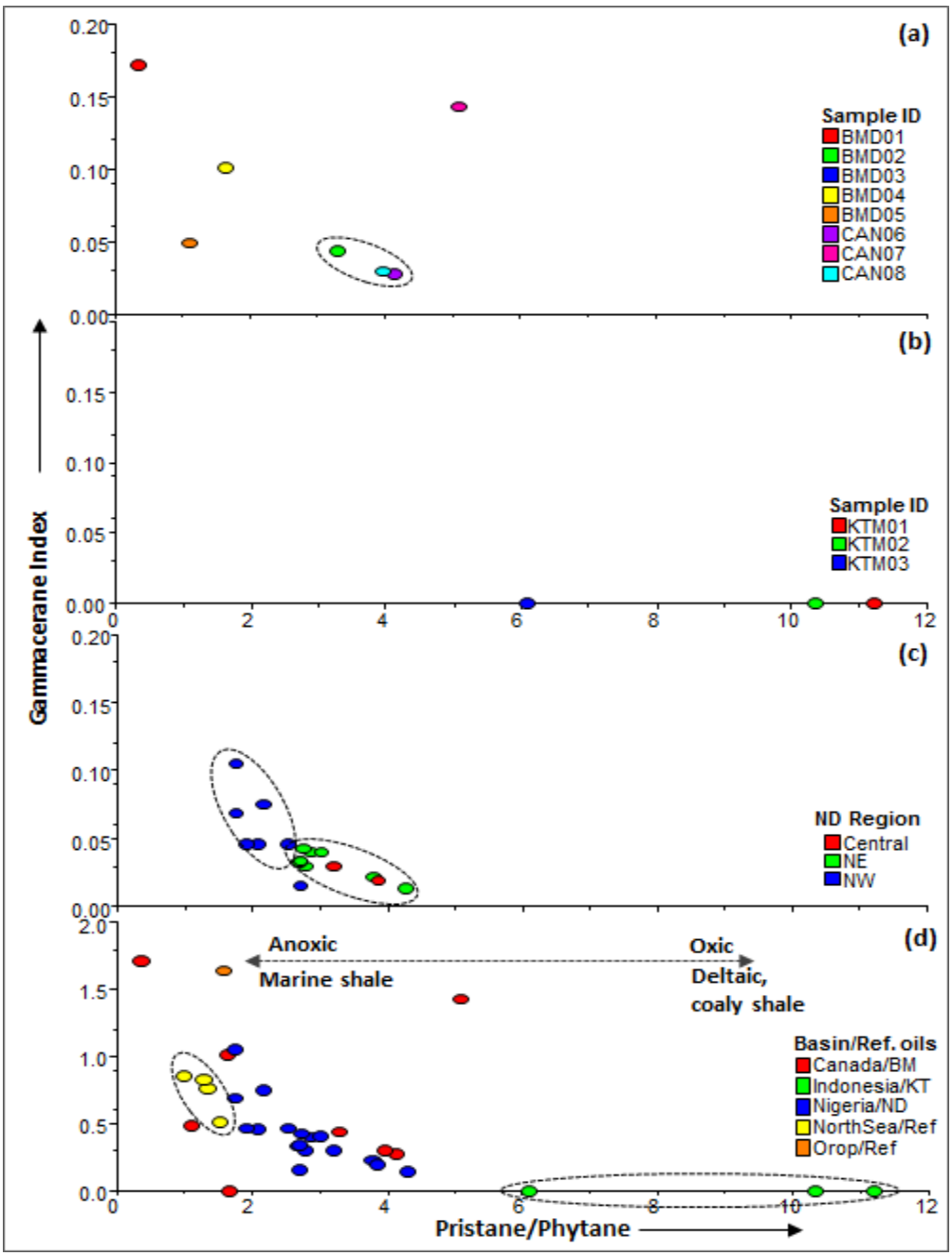


Figure 4.7 Cross plots of Pr/Ph ratios against gammacerane indices for: a) the Beaufort-Mackenzie delta oils; b) the Kutei Basin oils; c) classification for the 3 studied sections of the Niger Delta; note the grouping of some western oils with the eastern samples, which is suggestive of similar depositional conditions; and d) all study samples;. Oils are separated into families consistent with their depositional environments and organic matter source; note how these groupings compare to the marine reference oils. Gammacerane identification in these samples is tentative.

Samples that are grouped closer to the reference oils, with considerable amounts of gammacerane or higher, and relatively low Pr/Ph values, are believed to be derived from marine or mixed (marine/terrestrial) sources, but have, most likely, been reservoired in Tertiary sands of their respective formation. On the other hand, samples with very low or nil gammacerane index (high oleanane index) and high Pr/Ph ratios (>3-10), as could be seen with many oils of the Niger Delta (Eastern and Central regions) and the Kutei oils, are sourced from deltaic shale which have been deposited in increasingly oxic environment. It

should be noted, however, that the identification of gammacerane in the field samples were based on comparisons of their mass spectra and relative retention times with those of standards in the Chemstation library and component peaks in published data (e.g. Peters and Moldowan, 1993), and, hence, is tentative.

In general, the high relative abundance of oleananes in most samples is significant because oleanane is an indicator of higher plant source input and has long been attributed to angiosperm input to Tertiary or Cretaceous source rocks in deltaic sequences (Ekweozor *et al.*, 1979a, Hoffman *et al.*, 1984, Riva *et al.*, 1988). And, as would be expected for the first basin to be recognized for the abundance of terrigenous triterpenoids (Ekweozor *et al.*, 1979b) and oleananes (Whitehead, 1973), the Niger Delta oils exhibit the highest concentration of this organic–input and age-specific biomarkers amongst other deltaic oils. However, considerable amounts of these terrigenous markers were also detected in a couple of the reference marine oils (TRO01 and NSA02); though with relatively low oleanane abundance (<0.2; Table 4.3), an indication of a predominantly marine environment mixed by limited terrestrial contribution. Other terpenoid parameters, such as 30/29, H-Hop and 35/34 (Table 4.3) distinguished them from the 'non-marine' case study oils. The terpane maturity ratios (e.g. Hop32αβ*S*, Ts/Tm and C_{29}Ts/Tm; Table 4.3) confirm that these oils (reference) are highly mature.

4.2.4. *Aromatic Hydrocarbon Compounds*

Aromatic hydrocarbon fractions were isolated according to procedures described in the previous chapter (methodology). A number of polycyclic aromatic compound including naphthalenes, phenanthrenes, and dibenzothiophenes, were identified in most of the oils. These compounds were quantified and used to derive useful correlation and thermal maturity assessment parameters. (e.g. Radke, 1988a). For the purpose of peak identification and showing the distribution of aromatic hydrocarbons in a typical Tertiary oil in the sample set, Figure 4.8, Figure 4.9, and Figure 4.10 show typical distributions for phenanthrenes, naphthalenes, and dibenzothiophenes, respectively, in representative case study oils. Peak identification for all detected aromatic hydrocarbons is shown in Appendix II-g.

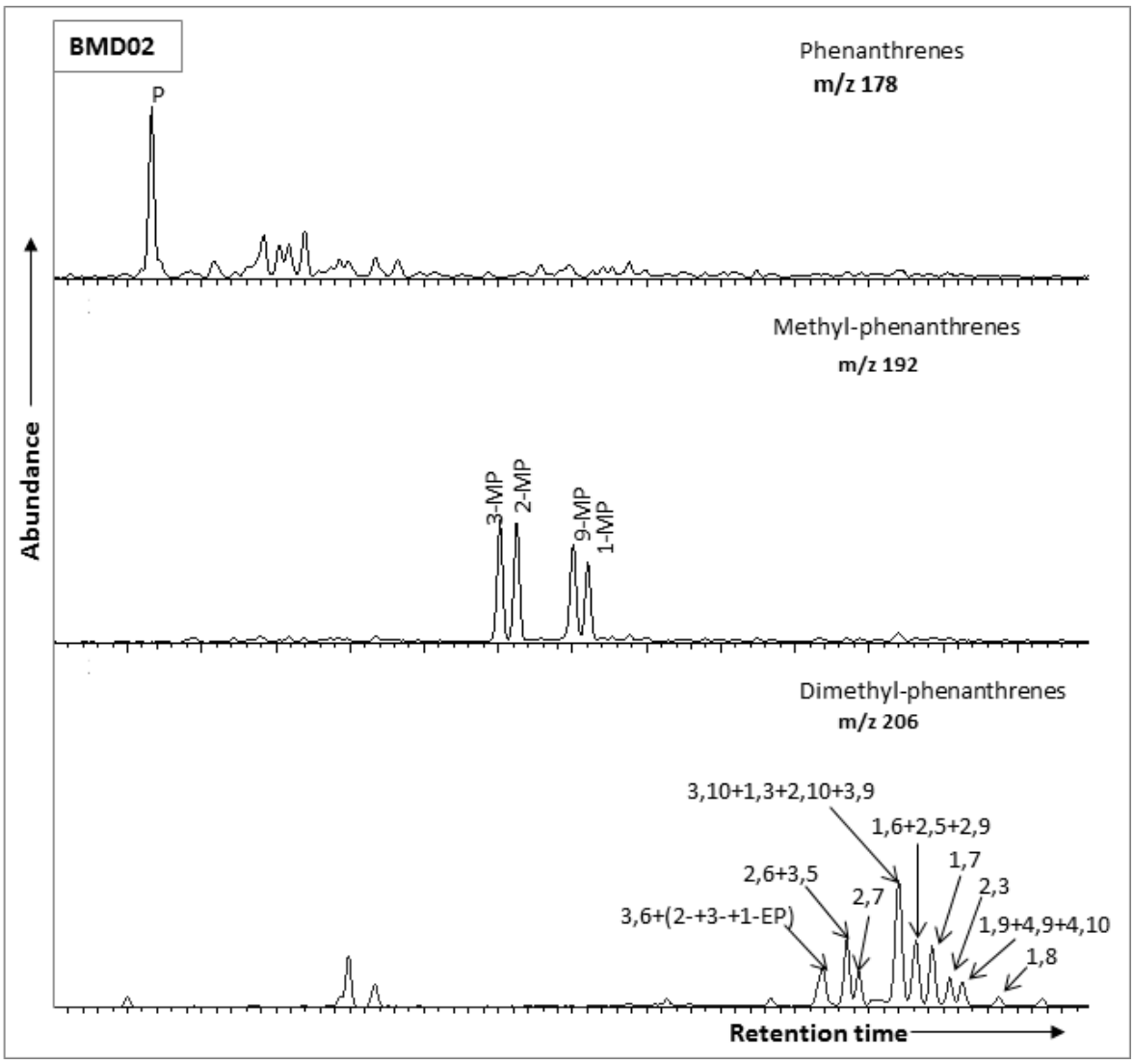


Figure 4.8 m/z 178, 192, 206 mass chromatograms showing the distributions of phenanthrene (P), methylphenanthrenes (MP), and dimethyl phenanthrenes (DMP) in the aromatic fraction of a representative Beaufort-Mackenzie oil (BMD02); EP are ethylphenanthrenes whose isomers (2-, 3-, and 1-EP) could co-elute with the DMP (e.g. 3,6-DMP). Numbers denote the position of alkyl- substitution on the parent aromatic ring.

Measured maturity parameters from the aromatic hydrocarbon compounds in the study oils from all three deltaic basins are presented in Table 4.4. Of particular interest in the distribution of these aromatic compounds within the Tertiary oils is the remarkable abundance of relatively high molecular weight aromatics in the Kutei oils as opposed to those (low to zero concentrations) of the steranes and terpanes in this oil set. Since aromatic hydrocarbons, as well as saturate hydrocarbon biomarkers, have been successfully applied as tools for oil characterisation, generated aromatic data (Table 4.4) enables the assessment of the thermal maturity of such oils as those of the Kutei Basin whose poor biomarker content made this initially impracticable. The aromatic data revealed that the Kutei oils are relatively mature.

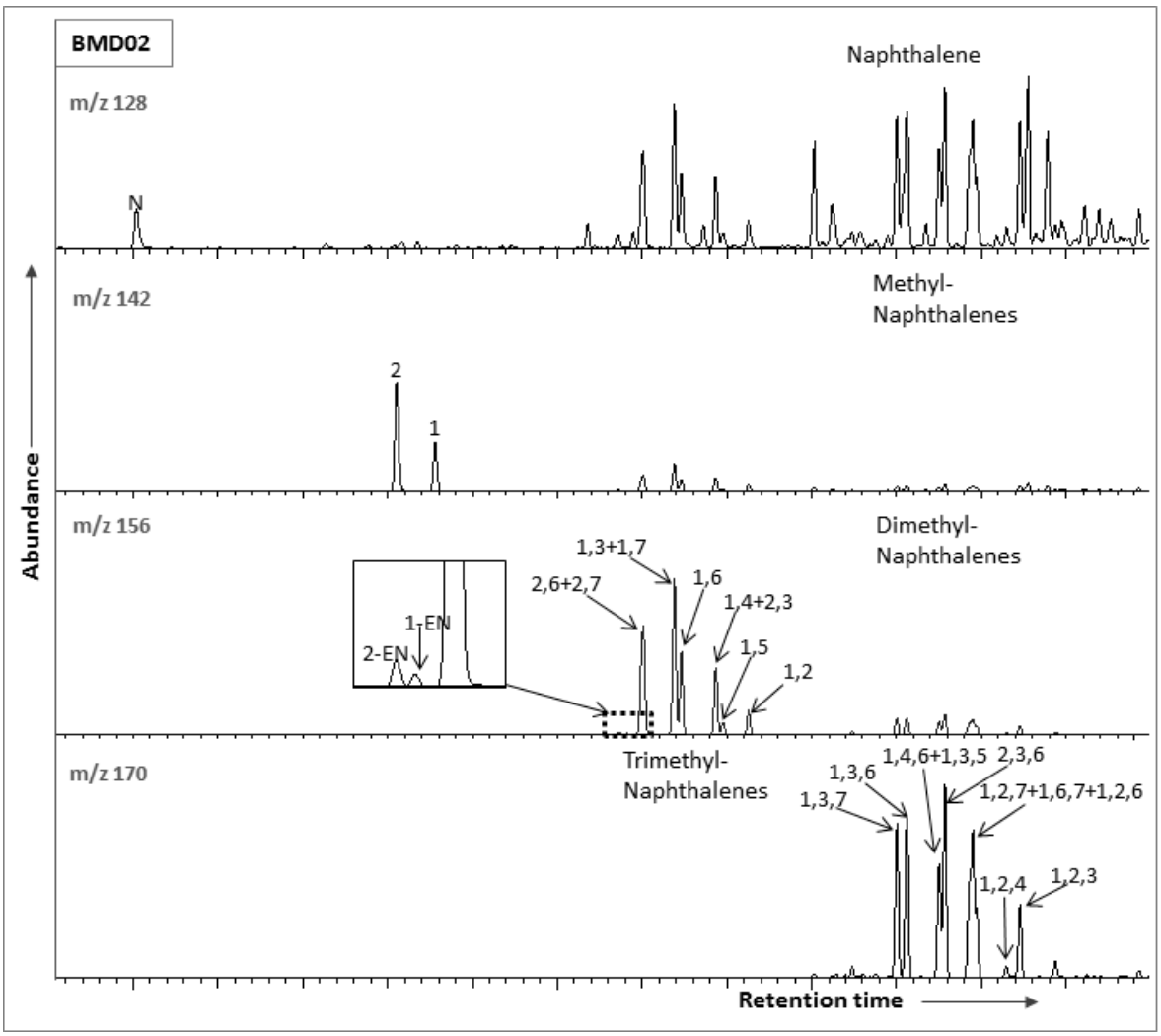


Figure 4.9 m/z 128, 142, 156, and 170 mass chromatograms showing the distributions of naphthalene, methylnaphthalenes, dimethylnaphthalenes and trimethylnaphthalenes, respectively, in a representative oil (BMD02) from the Beaufort-Mackenzie Delta. 'EN' denotes ethyl-naphthalenes which are shown (enlarged) to elute just before the DMN. The integers signify the carbon position of alkyl substitution.

The MethylPhenanthrene Index (MPI) is one of the most frequently applied aromatic maturity parameters. Both MPI-1 and -2 versions are derived from phenanthrene and isomers of methylphenanthrenes, and vary proportionally to each other in every sample. Table 4.4 shows the values of MP1-1 and MPI-2 for the oils, ranging from 0.46-1.67 and 0.57-1.90 (Beaufort-Mackenzie), 0.49-0.78 and 0.51-0.76 (Kutei Basin) and 0.75-1.11 and 0.80-1.13 (Niger Delta), respectively. The equivalent vitrinite reflectance value (%Rc) for crude oils was calculated using MPI-1 (Table 4.4) from its linear correlation with conventionally measured vitrinite reflectance (Radke *et al.*, 1982). A plot of MPI-2 vs MPI-1 (Figure 4.11b) show very good correlation between the two parameters, with increasing maturity.

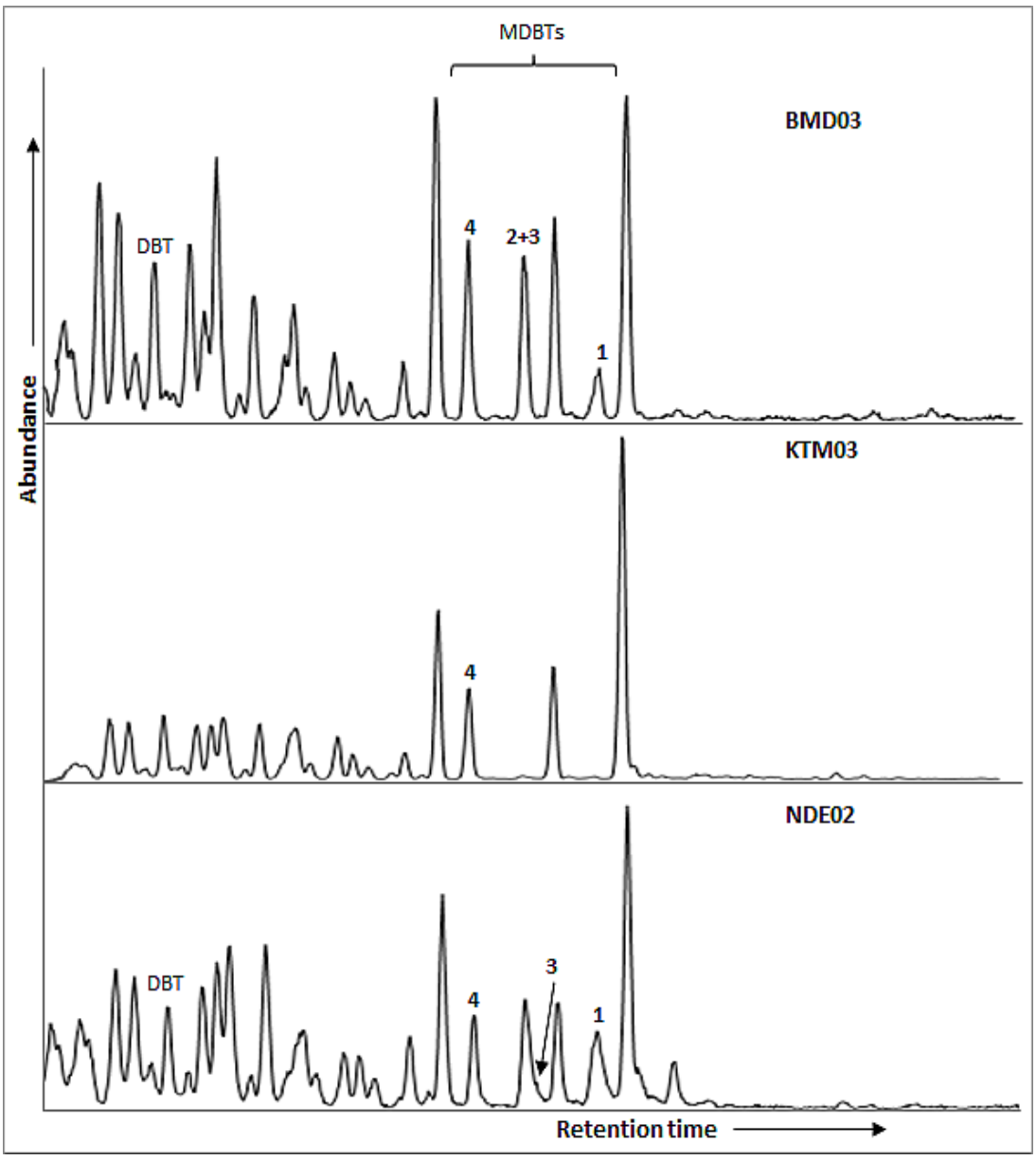


Figure 4.10 Representative combined m/z 184+198 mass chromatograms showing the distribution of dibenzothiophene (DBT), and its methyl derivatives (MDBTs) in aromatic fractions of BMD03, KTM03 and NDE02 representing oil from the 3 study basins.; MDBTs = methyldibenzothiophene (4-, 2-, 3-, and 1-isomers). 2-MDBT co-eluted with 3-MDBT in many of the samples.

The DNR-1 (DMNR) and DNR-2 ratios were calculated from the dimethylnaphthalene (DMN) distributions in the oils (e.g. Radke *et al.*, 1982, Radke *et al.*, 1986), and range from 0.77-3.18 and 0.85 to 2.83 (Beaufort-Mackenzie Delta); 2.53-15.01 and 1.8-2.54 (Kutei Basin) and; 4.71-25.24 and 1.98-3.30 (Niger Delta) respectively (Table 4.4; Appendix III-b). A cross plot of DNR-2 vs. DNR-1 (Figure 4.11a) illustrates a positive correlation between both ratios.

Table 4.4 Selected aromatic maturity and source parameters measured in the studied oil samples.

Sample	MPI(1)	MPI(2)	MNR	DNR-1	DNR-2	ENR	Rc: Ro<1.35	Rc: Ro>1.35	MPR	DBT/P	3/2MB	TMNR-2
BMD01	0.49	0.68	1.68	2.39	0.85	0.77	0.69	2.01	2.41	0.27	1.98	0.53
BMD02	0.94	0.94	2.28	12.05	2.15	1.51	0.96	1.74	1.55	0.01	10.64	0.68
BMD03	0.98	1.03	2.33	14.72	2.83	3.04	0.99	1.71	1.32	0.01	21.28	0.86
BMD04	0.79	0.70	1.43	5.61	1.83	1.87	0.87	1.83	0.84	0.01	3.70	0.68
BMD05	1.67	1.90	1.62	6.12	2.69	3.18	1.40	1.30	2.26	0.03	11.78	0.66
CAN06	0.46	0.53	2.06	10.43	1.65	1.94	0.68	2.02	0.89	0.02	26.87	0.55
CAN07	0.54	0.57	0.83	4.06	0.96	1.30	0.72	1.98	1.06	0.18	1.27	0.74
CAN08	0.52	0.58	1.57	9.45	1.52	2.56	0.71	1.99	0.87	0.04	20.88	0.56
KTM01	0.71	0.74	1.79	13.34	2.01	0.00	0.83	1.87	1.43	0.09	20.61	0.54
KTM02	0.49	0.51	1.62	2.53	1.80	0.00	0.69	2.01	1.42	0.06	13.78	0.65
KTM03	0.78	0.76	2.15	15.01	2.54	2.55	0.87	1.83	1.35	0.04	39.03	0.66
NDE01	0.96	0.94	2.00	11.19	2.05	2.39	0.98	1.72	1.26	0.01	15.25	0.66
NDE02	0.81	0.87	1.91	8.44	2.58	1.21	0.89	1.81	1.05	0.13	12.08	0.66
NDE03	0.92	1.00	1.63	8.32	2.60	1.58	0.95	1.75	1.25	0.17	10.83	0.62
NDE04	0.82	0.89	1.84	6.56	3.03	1.86	0.89	1.81	1.18	0.17	13.14	0.67
NDE05	0.75	0.80	1.49	4.71	2.51	1.29	0.85	1.85	0.97	0.24	17.04	0.55
NDE06	0.87	0.92	1.28	5.18	2.38	1.04	0.92	1.78	1.05	0.25	12.90	0.59
NDE07	0.75	0.82	2.01	6.12	2.83	1.09	0.85	1.85	0.83	0.27	8.64	0.57
NDE08	0.89	0.90	1.57	7.78	2.58	2.42	0.93	1.77	1.14	0.10	14.34	0.58
NDW09	0.81	0.96	1.94	8.01	3.30	1.41	0.89	1.81	0.94	0.04	14.74	0.67
NDW10	0.77	0.86	1.82	7.59	3.17	1.30	0.86	1.84	0.98	0.07	14.01	0.61
NDW11	0.88	0.88	1.95	9.78	2.45	2.53	0.93	1.77	1.23	0.02	3.34	0.66
NDW12	1.06	1.03	2.11	18.25	2.25	2.95	1.04	1.66	1.45	0.04	18.58	0.64
NDW13	0.96	1.07	1.49	6.42	3.09	1.79	0.97	1.73	1.29	0.18	5.36	0.62
NDW14	0.95	1.02	2.45	9.79	2.96	1.05	0.97	1.73	1.36	0.03	10.95	0.72
NDW15	0.87	0.93	2.33	12.20	3.25	1.37	0.92	1.78	1.30	0.02	25.57	0.67
NDC16	0.90	0.93	1.48	8.50	2.44	1.30	0.94	1.76	1.46	0.03	50.71	0.63
NDC17	1.11	1.13	2.40	25.24	1.98	0.00	1.06	1.64	1.49	0.03	35.16	0.61
TRO01	1.14	0.97	2.74	18.13	2.23	3.35	1.08	1.62	1.33	0.04	19.96	0.78
NSA02	0.72	0.72	1.58	5.21	1.04	0.00	0.83	1.87	1.13	0.22	7.91	0.61
NSA03	0.84	0.87	2.07	11.98	1.90	2.89	0.90	1.80	0.88	0.02	8.02	0.75
NSA04	0.62	0.61	1.59	6.27	2.42	4.16	0.77	1.93	0.90	0.07	5.53	0.77
NSV05	0.71	0.75	1.75	9.76	1.79	2.82	0.83	1.87	0.92	0.02	9.95	0.62

MPI-l= 1.5*(2-MP+ 3-MP)/ (P + I-MP + 9-MP) (Radke *et al.*, 1982); MPI-2 = (3* 2-MP)/(P+ I-MP + 9-MP) (Radke *et al.*, 1982); MNR = (2-MN/1-MN); DNR-l (also DMNR) = (2,6-DMN+ 2,7-DMN)/l,5-DMN; DNR-2 = (2,6-DMN+2,7-DMN)/(1,4-+2,3-)DMN; ENR = 2-EN/I-EN; Rc(Ro<1.35) = (0.6*MPI-1)+0.4 and Rc(Ro>1.35) = (-0.6*MPI-1)+2.3 are Vitrinite reflectance value calculated from MPI(1) for values less than or greater than 1.35% Reflectance respectively (Radke *et al.*, 1982); MPR = 2-MP/1-MP; ; DBT/P = dibenzothiophenes/phenanthrene (Radke *et al.*, 1982); 3/2MB = 3-methyl / 2-methylbiphenyl from GC-MS m/z 168; TMNR-2 = 1,3,7-TMN/(1,3,7-TMN+1,2,5-TMN) (Sonibare *et al.*, 2008); nil values means ratio could not be measured due to very low amounts or absence of one or more compounds. The reference oils are greyed.

The occurrence of dibenzothiophene (DBT) and its alkyl derivatives find application in the assessment of paleoenvironment and maturity. The distributions of the dibenzothiophenes and methyl-dibenzothiophenes in three representative oils are shown in Figure 4.10. The four isomers of methyl-dibenzothiophene (4-, 2-, 3-, and 1-MDBT) were identified in most oils. 2-MDBT usually co-eluted with the least prominent (or even absent) 3-MDBT in many of the samples. This distribution suggests that the oils are of relatively low thermal maturity (e.g. Hughes *et al.*, 1995). The relative abundance of dibenzothiophene compared to

phenanthrene (DBT/P ratio) has been derived for the study samples (Table 4.4). The DBT/P ratios range from 0.04-0.09 for the Kutei oils and 0.01-0.27 for the Beaufort-Mackenzie and Niger Delta oils and is used here to indicate source rock depositional environment for these oils. This ratio is <1 for all the study oils; a clear indication that they are not generated from carbonate-rich source rocks (Hughes *et al.*, 1995). According to Hughes *et al.* (1995), a cross-plot of dibenzothiophene/phenanthrene versus the pristane/phytane ratios (discussed in a later section) provides a tool for inference of source rock depositional environments and lithology.

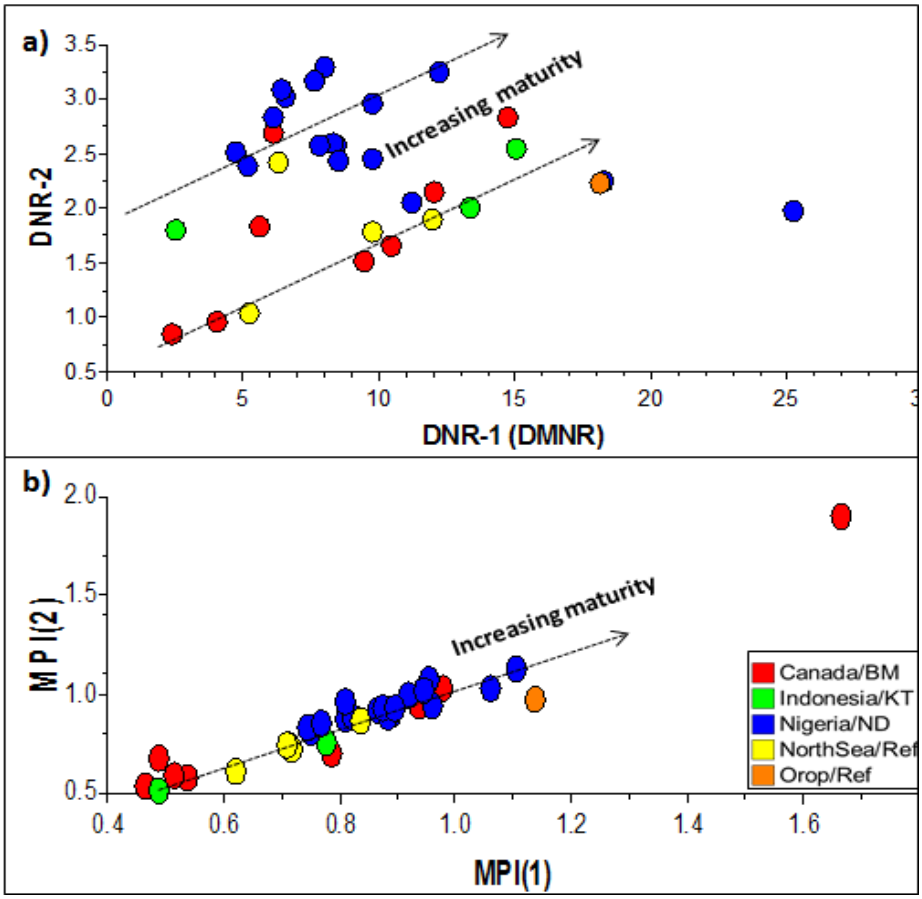


Figure 4.11 Cross plots of two pairs of thermal maturity parameters: a) DNR-2 vs DNR-1 and b) MPI-2 vs MPI-1; derived from aromatic hydrocarbon data for all the analysed oils. Note the positive correlation between these parameters, enabling the establishment of applicable maturity trends (after Sonibare *et al.*, 2008).

4.2.5. *Aromatic Steroid Hydrocarbons*

The triaromatic steroid (TAS) amounts and distributions were obtained from the m/z 231 mass chromatograms of whole aromatic fractions while the monoaromatic steroid data was derived from isolated monoaromatic steroid (MAS) hydrocarbon fraction from whole aliphatic hydrocarbon fraction by TLC, as described in the previous chapter (Figure 3.2). Unlike the TAS hydrocarbons, no standards were added to the MAS fractions prior GC and

GC-MS analysis; hence actual concentration of MAS hydrocarbons were not quantitated. However, derived MAS ratios were calculated using integrated peak areas of respective components in the samples. The two groups of compounds were analysed in different fractions (MAS and aromatic) but each fraction was made up to the same analyte volume as the other, and same volume of each was auto-injected onto the instrument. Hence, ratios which include TAS and MAS components are approximate values, and are derived, only, for the purpose of comparisons. In addition, since the MAS and TAS compounds were detected using two different mass chromatograms (m/z 253 and 231), relative abundance ratios and parameters of both compound classes were calculated using areas of corresponding component peaks of TAS (m/z 231.117) and MAS (m/z 253.196) peaks with no response factors.

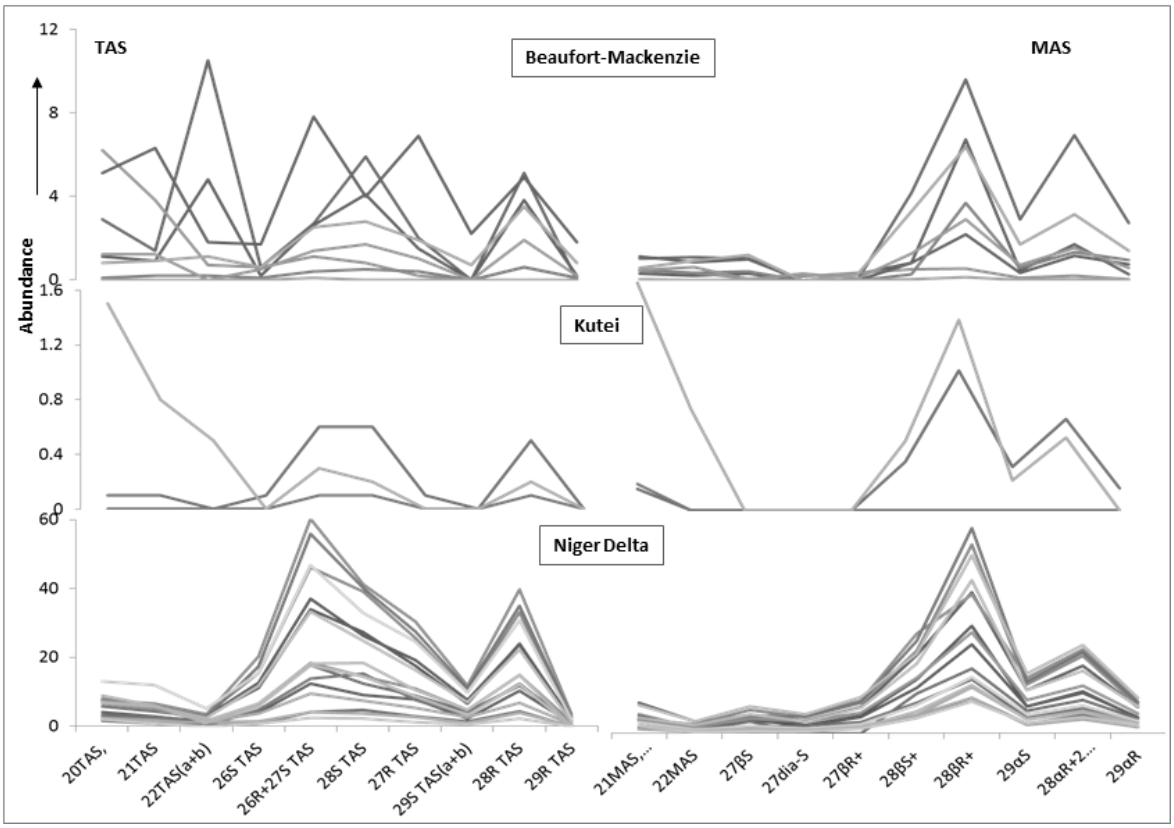


Figure 4.12 General overview of the distribution of the aromatic steroid hydrocarbons in the three sample subsets as shown. Note the relatively high abundance of TAS in the Niger Delta oils and the similarity of distributions within these oils for both TAS and MAS groups. The distributions are more similar within sample sets for MAS than TAS hydrocarbons.

Monoaromatic Steroid (MAS) Hydrocarbons

The distributions of monoaromatic steroids within the oils in all three sample sets were generally similar (Figure 4.12). Representative m/z 253 mass chromatograms of typical oils showing the distribution of MAS hydrocarbon, ranging from C_{27}-C_{29}, are shown in Figure

4.13. The distributions are dominated by the C_{28} and C_{29} components. As mentioned earlier, concentrations of identified MAS components were not measured, but peak ratios were measured from relevant peak areas to estimate relative abundances and distributions in the oils. In the Kutei oils, the MAS components occur in low to unmeasurable concentrations in relation to other samples. While C_{29} and C_{28} species dominate the distribution in the Niger Delta sample set, C_{28} components are generally dominant in the Beaufort-Mackenzie oils (Figure 4.13). In addition to having the most consistent distributions across samples, the Niger Delta oils generally exhibit the largest number of identified MAS components across the sample subsets (Figure 4.12; Figure 4.13).

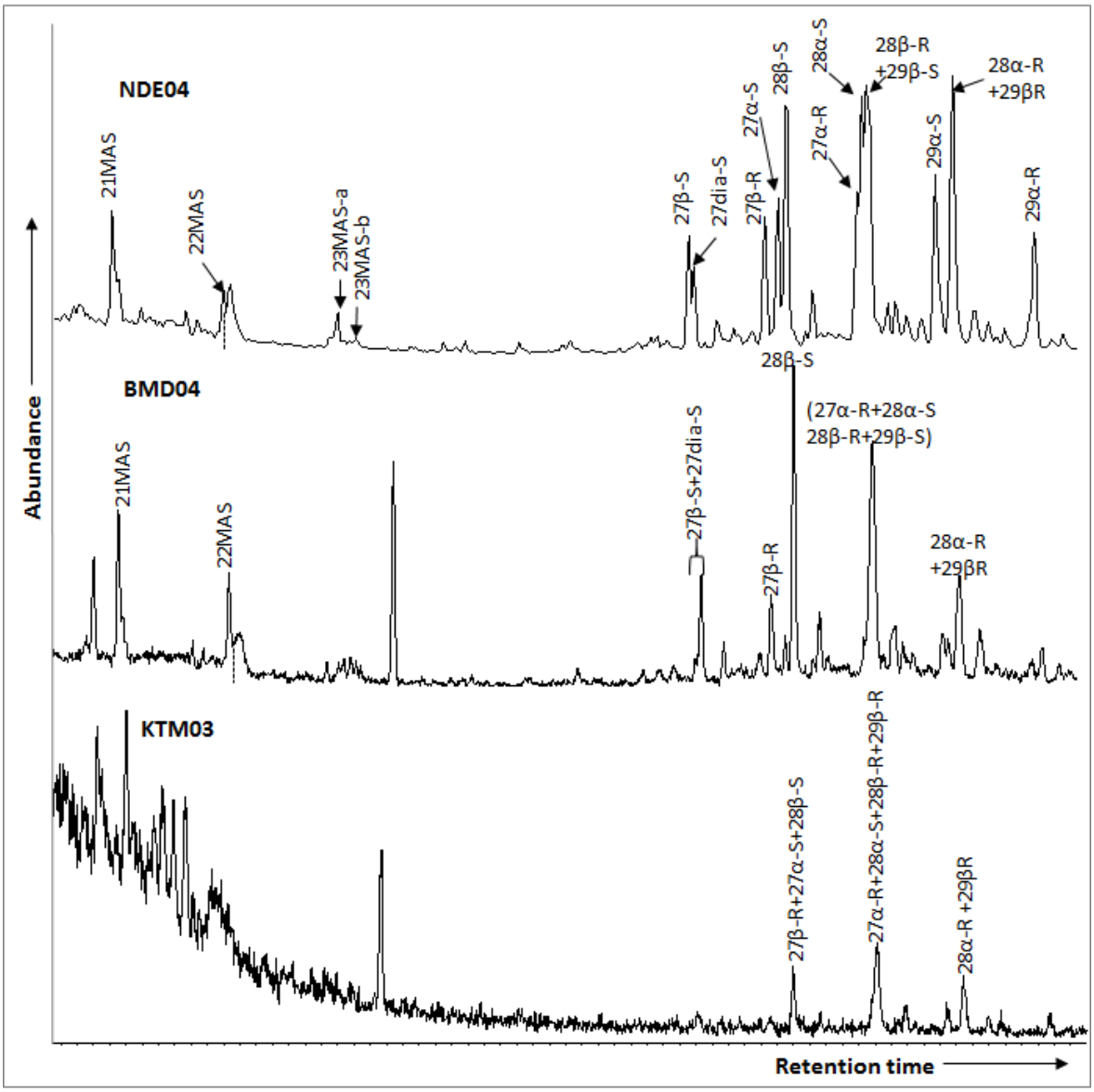


Figure 4.13 m/z 253 mass chromatograms showing distribution of monoaromatic steroid HCs from MAS fractions of representative Tertiary oils: NDE04, BMD04 and KTM03. 'a' and 'b' of 23MAS are epimeric at C_{20}. Note the relatively low abundance of the C_{27}-C_{29} components in a typical Kutei oil (KTM03).

Tri-aromatic steroid (TAS) hydrocarbons

The triaromatic steroid (TAS) hydrocarbons dominate the aromatic steroid hydrocarbon fractions of most oils. Figure 4.14 shows the distribution of the TAS hydrocarbons in representative m/z 231 mass chromatograms. The distribution is even wider ranging than that of the MAS, from C_{26}-C_{29} with more significant amounts of C_{26} and C_{27} groups as well as C_{28} species dominating the TAS components in most samples. The preponderance of TAS compounds over MAS was proposed by Mackenzie *et al.* (1981) as being the consequence of an aromatisation process involving the loss of one carbon atom from the MAS compound during maturation. However, this was also later tentatively attributed to a migration effect (Hoffman *et al.*, 1984).

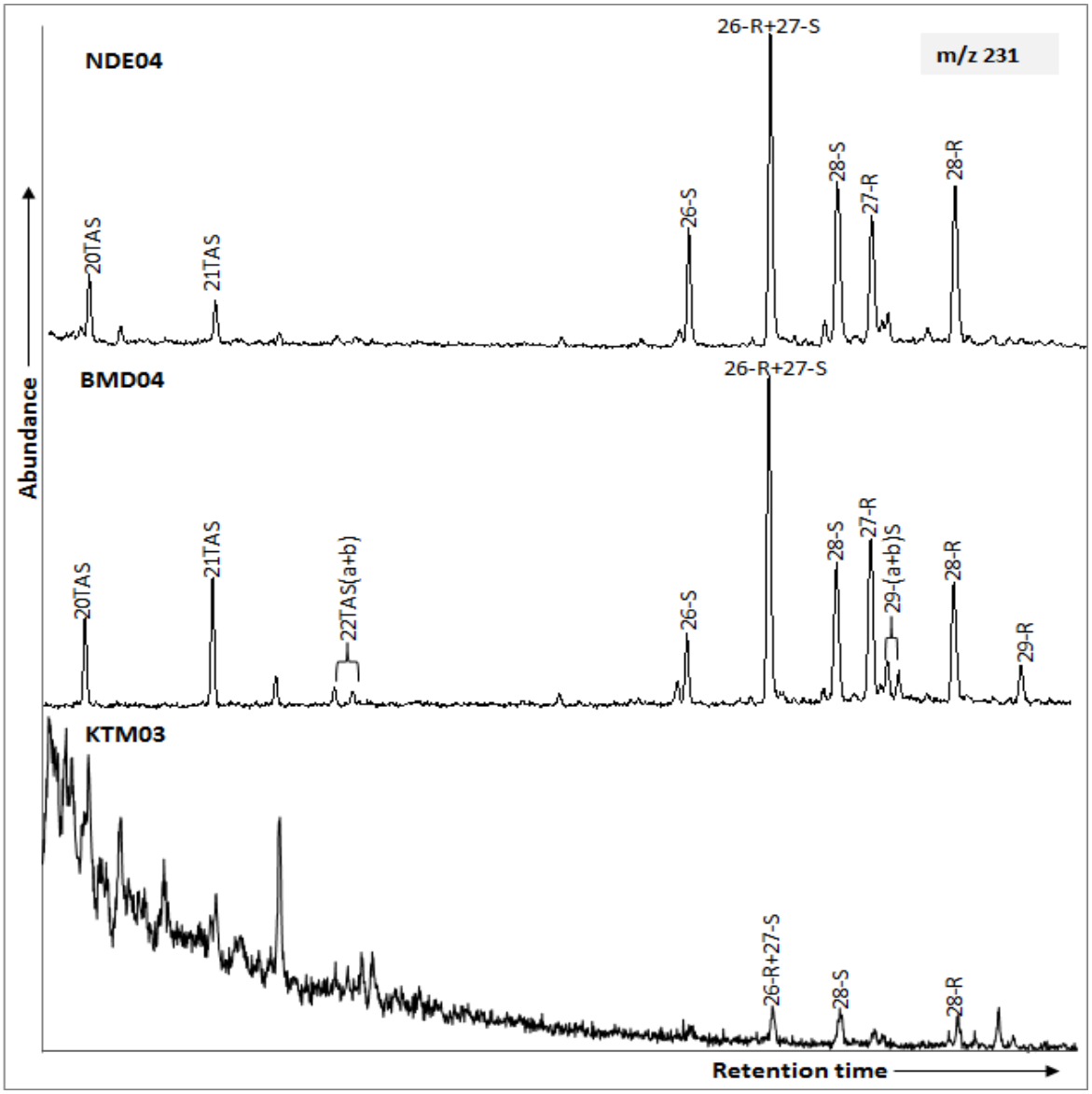


Figure 4.14 Mass chromatograms (m/z 231) showing TAS hydrocarbons from representative oil samples for each of the Tertiary deltaic basins studied. The peak names are abbreviated and shown to include the carbon numbers that make up the compounds; S or R denote diastereoisomers 20*S* and 20*R*; 'a' and 'b' represent twin epimers at C_{20} of corresponding TAS compound (in BMD04).

The aromatic steroid hydrocarbon parameters measured are shown in Table 4.5. The TAS%C_{26}-C_{28} parameters relative to the sum of concentrations of all three homologues range widely for Beaufort-Mackenzie oils based on analysed samples. They are fairly consistent in the Kutei oils but the Niger Delta oils, again, revealed a closer ranging and more uniform distribution (average: 21%C_{26}, 35%C_{27}, and 44%C_{28}; Table 4.5). Similar to the steranes, a triangular plot of %TAS distribution (Figure 4.15) was applied for source assessments and it could be observed that the Niger Delta and Kutei Basin oils each appeared as coming from the same source within their individual setting but the Beaufort-Mackenzie oils, as earlier evidenced, appeared to be of mixed origins.

Table 4.5 Aromatic steroid (MAS/TAS) hydrocarbon parameters for the studied oils.

Sample	M21+22/tot	M29S/R	T20+21/tot	T28S/R	%T26	%T27	%T28	ST	M29R/T28R	T21	% TAS
BMD01	0.08	1.07	0.26	1.17	6.37	25.58	68.04	169.50	30.71	0.22	47.16
BMD02	0.09	0.47	0.17	1.08	8.78	30.09	61.13	30.28	3.31	0.19	95.04
BMD03	0.39	1.94	2.99	1.32	37.18	23.38	39.43	20.71	0.40	0.86	98.46
BMD04	0.18	1.60	0.45	0.82	15.02	49.72	35.26	152.28	1.14	0.56	93.78
BMD05	0.12	0.61	0.15	0.84	8.81	32.14	59.06	8.86	67.19	0.22	26.28
CAN06	0.15	1.27	0.05	1.37	9.48	32.82	57.70	187.09	1.92	0.10	95.16
CAN07	0.17	1.19	0.12	2.23	2.25	52.64	45.11	354.39	4.03	0.32	92.00
CAN08	0.09	1.21	0.03	1.43	11.68	38.42	49.91	271.59	2.88	0.08	93.81
KTM01	n.m	n.m	n.m	1.33	22.42	22.42	55.16	n.m	n.m	n.m	100.00
KTM02	0.06	1.98	0.10	1.28	24.00	27.16	48.84	n.m	0.17	0.21	99.28
KTM03	0.91	n.m	2.78	1.00	28.77	28.77	42.45	n.m	n.m	0.76	97.82
NDE01	0.10	1.66	0.16	0.89	21.38	35.22	43.40	16.63	2.32	0.21	94.22
NDE02	0.08	1.62	0.12	1.14	21.20	35.33	43.47	75.96	0.27	0.21	99.32
NDE03	0.05	1.76	0.09	1.18	19.35	36.13	44.52	96.61	0.53	0.14	98.53
NDE04	0.06	1.75	0.11	1.11	22.93	36.37	40.69	87.78	0.24	0.20	99.36
NDE05	0.08	1.49	0.09	1.23	17.00	32.09	50.91	33.29	0.08	0.15	99.77
NDE06	0.05	1.73	0.07	1.04	24.34	35.37	40.30	163.50	0.70	0.14	98.19
NDE07	0.04	1.71	0.06	1.15	22.51	36.88	40.61	161.69	0.70	0.11	98.16
NDE08	0.05	1.51	0.15	1.08	11.84	34.94	53.22	4.25	28.24	0.15	53.01
NDW09	0.06	1.31	0.16	1.10	22.41	34.59	43.00	25.20	0.11	0.24	99.77
NDW10	0.06	1.36	0.11	1.06	24.14	35.34	40.53	36.50	0.18	0.19	99.62
NDW11	0.06	1.69	0.18	0.97	21.59	34.21	44.19	75.04	2.53	0.26	94.06
NDW12	0.13	1.30	0.22	0.93	19.31	33.36	47.34	6.83	0.20	0.24	99.60
NDW13	0.08	1.69	0.12	1.11	23.94	34.33	41.73	56.13	1.53	0.21	96.25
NDW14	0.06	1.63	0.17	1.07	23.03	36.30	40.67	100.39	0.51	0.28	98.81
NDW15	0.09	1.54	0.22	1.19	21.71	34.90	43.38	36.20	0.17	0.33	99.62
NDC16	0.08	1.73	0.22	1.23	17.40	34.08	48.52	148.11	0.13	0.29	99.66
NDC17	0.10	1.28	0.32	1.00	21.03	31.25	47.72	12.14	0.26	0.29	99.49
TRO01	0.14	1.79	0.61	0.79	19.19	42.37	38.44	24.21	0.21	0.54	99.38
NSA02	0.10	1.00	0.32	0.89	19.79	42.28	37.93	168.35	2.82	0.44	87.89
NSA03	0.50	1.38	0.57	1.16	15.04	46.53	38.43	44.62	0.08	0.60	99.15
NSA04	0.41	0.94	0.13	1.91	21.92	41.54	36.55	796.55	0.93	0.39	93.96
NSV05	0.37	1.29	0.17	1.47	15.57	38.09	46.34	70.61	0.17	0.37	98.93

M21+22/tot=(MAS21+MAS22)/(MAS-27β20*S*+DiaMAS27-20*S*+MAS-27β20*R*$^{+}$+MAS-28β20*S*$^{+}$+MAS-28β20*R*$^{+}$+MAS-29α20*S*+MAS29β20*R*$^{+}$+MAS29α20*R*); M29*S*/*R* = (MAS29α20*S*/MAS29α20*R*); T20+21/tot = (TAS20/TAS21)/(TAS26-20*S* + TAS26-20*R*$^{+\ \mathrm{TAS27\text{-}20}S}$ +TAS28-20*S* + TAS27-20*R* + TAS28-20*R*); T28*S*/*R* =

TAS28-20*S*/TAS28-20*R*; %T26, %T27 and %T28= T26, T27, T28 as % of sum C_{26-28} (20*R*+*S*) TAS; ST = Sum((C_{27}(20*R*+*S*) diasteranes)+(C_{29}-ααα+αββ (20*R*+*S*) steranes))/((Sum(C_{27}-29α+β(20*R*+*S*) MAS & diaMAS)+Sum(C_{26-28}(20*R*+*S*) TAS)); M29R/T28*R*(%) =MAS29-5α20*R*/(MAS29-5α20*R*+TAS28-20*R*); T21 =TAS21/(TAS21+TAS28)-20*R*; %TAS = (TAS28/(TAS28+MAS29-β)-20*R*)*100. n.m = not determined due to very low amounts or absence of one or more compounds within the formula. Superscripted components include possible co-eluting compounds. The reference oils are greyed.

The variation in distribution of TAS components in the oils of the Beaufort-Mackenzie Delta indicated both varied depositional environments and organic matter sources. Although the Niger Delta oils contain the highest relative concentrations of total TAS, they exhibited a fairly similar distribution to those of many Beaufort-Mackenzie oils. Analogous to their MAS components content, the Kutei oils are not rich in the TAS hydrocarbons.

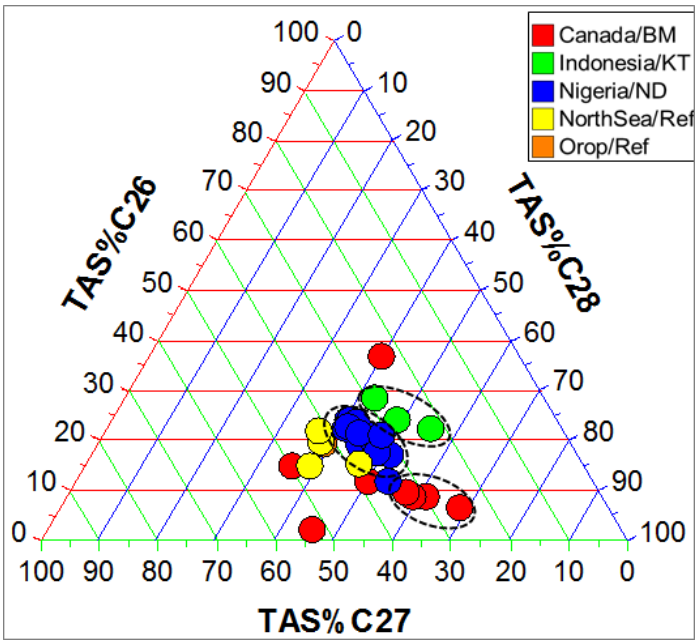


Figure 4.15 Triplot of C_{26}-C_{28} TAS components showing the distributions indicating source-type relationships of oils families.

4.3.Summary of Oil Sample Source Facies and Thermal Maturities

Although reservoired within the Tertiary sands of various formations within the basin (Dixon *et al.*, 1992), the studied Beaufort-Mackenzie crude oil samples showed molecular properties that clearly separated them into marine and terrestrially sourced oils. This implies expulsion from sources rocks with two different kerogen types. These observations are in agreement with past published findings on the typical two end member organofacies characteristics of Beaufort-Mackenzie oil accumulations (e.g. Snowdon and Powell, 1979, Brooks, 1986a, Curiale, 1991). Both types of oils are evidently mature (Table 4.2 and Table 4.3), but the supposedly Cretaceous source rocks of the marine oils may be more thermally mature than the organic-rich Tertiary source units of the terrigenous oils.

Based on the relative abundance of oleananes, absence of steranes and overall molecular makeup of the three examined Kutei samples, these oil condensates must have been expelled by source rocks that had received abundant organic matter input from terrestrial higher plants. In addition, the exceptionally high Pr/Ph ratios (>6) and absence of gammacerane in the oils are indications of source rock organic matter accumulation in a relatively oxic environments (Figure 4.7; Figure 4.16; Figure 4.17). In terms of maturity, aromatic hydrocarbon parameters, such as calculated vitrinite reflectance, $\%R_c$, suggest mid-oil window for these oils at the time of expulsion. These source characteristics are typical of oils from deltaic source rock comprised mainly of terrigenous (type III kerogen) coaly shales.

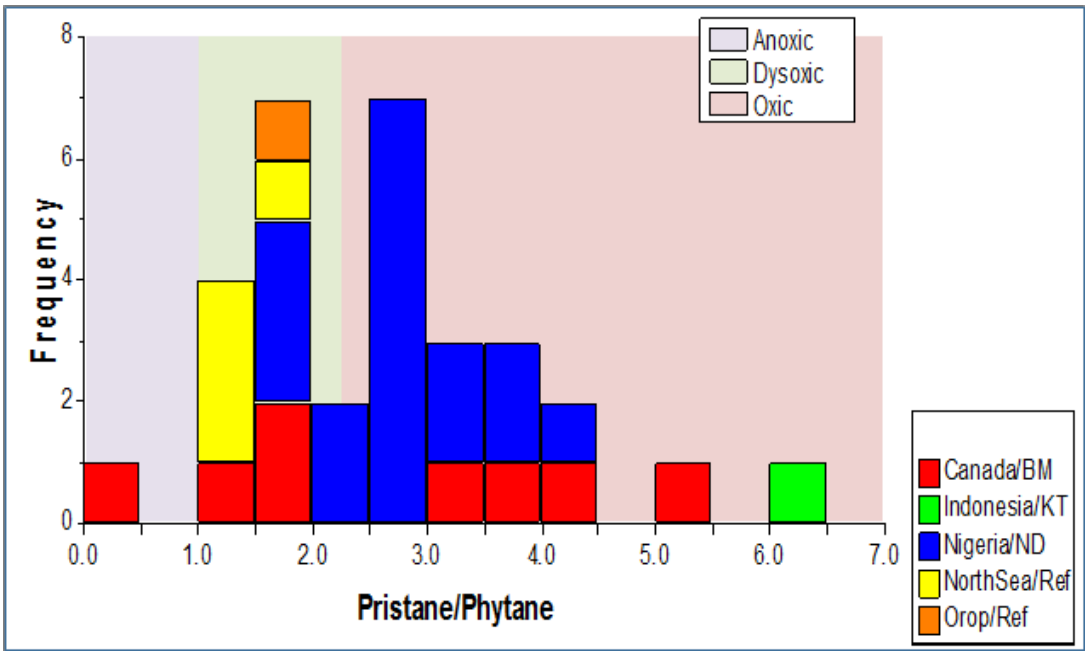


Figure 4.16 Source rock anoxia inferred from the pristane/phytane ratio. This plot shows the variable source depositional environments in a set of regionally similar oils. Here, there are two distinct distributions for oils of the Beaufort-Mackenzie DeIta. Plots overlaid using pIGI software.

Earlier published studies have observed three different oil families for the Niger Delta oils by integrating all sections of the Delta (e.g. Ekweozor *et al.*, 1979a, Haack *et al.*, 2000, Samuel *et al.*, 2009). This study summarises its findings based only on data derived from analysed sections. Measured molecular data (Table 4.1, Table 4.2, Table 4.3, and Table 4.6) showed the presence of one-end member and one intermediate oil family within the studied Niger Delta oil reservoirs. The occurrence of these oil families from two corresponding petroleum systems is a pointer to the existence of more than one major source kitchen. They include: a) mixed (marine/terrigenous) system comprising of source rocks that are deposited under less oxygenated environmental conditions; and b) terrigenous system dominated by extreme terrigenous characteristics. This is most common in shallow water accumulations,

particularly in the North-Western section of the delta (Samuel *et al.*, 2009). Figure 4.19 shows the shift in oxicity between the oils of the studied Niger Delta sections; the North-Eastern oils are deposited in more oxic conditions than the rest of the oils and these also show evidence of increasing angiosperm input to their source rocks, with consequent increasing oleanane index. There is also a possibility of charging from both end members of terrigenous and marine source rocks.

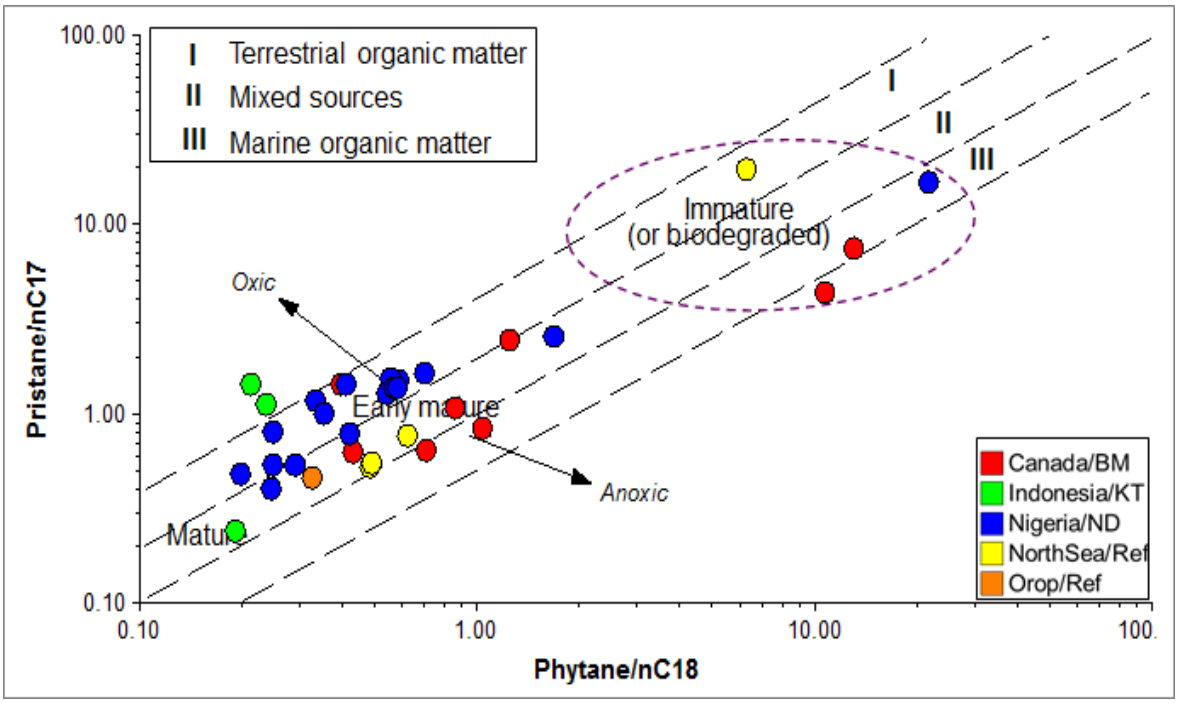


Figure 4.17 A plot of pristane/*n*-C_{17} vs. phytane/*n*-C_{18} ratios used to infer oil source rock anoxia. Special attention should be paid to the biodegraded oils in the sample set as these parameters generally increase in these oils and hence are sensitive to biodegradation. Overlays using pIGI software.

The dominantly terrigenous, Tertiary oils are widespread over the whole delta. Of the studied Niger Delta oils, many North-Eastern area oils show the most deltaic molecular properties (Table 4.1, Table 4.2 and Table 4.3) which include high oleanane index (1.16-2.05), high C_{29}-steranes and diasteranes (39.23-57.17%) and high Pr/Ph ratios (2.71-4.29).

4.4.Biomarker Signals in studied Oils and Source Implications

4.4.1. *Source Rock Depositional Environment and Lithology*

The sterane and diasterane ternary plots of respective (20*R*)-C_{27}: (20*R*)-C_{28}: (20*R*)-C_{29} homologues in Figure 4.3 show clustering towards the C_{29} apex. These attributes are used to confirm higher plant inputs to source rock deposition. The diasterane plot (topmost Figure 4.3) did not lend much separation to the samples as majority of these oils are non-biodegraded, with only a few severely and very slightly degraded ones, but some groupings

are still noticeable. A clear distinction between the analysed North Sea reference, and Tertiary deltaic oils on the plot highlights the differences in the depositional environments and source organic matter of both sample sets in this regards and this will be useful in the assessment of migration-contamination based on compositional differences.

Table 4.6 Summary of source and maturity parameters for the study oils.

Region		Sample	Pr/Ph	%C27	%C29	OL	Ts/Tm	MPI(1)	Possible Source
Beaufort-Mackenzie Delta		BMD01	0.36	34.96	47.95	0.85	0.68	0.49	Mixed
		BMD02	3.30	42.52	46.02	0.24	0.45	0.94	?Mixed
		BMD03	1.66	n.d	n.d	n.d	n.d	0.98	?Mixed
		BMD04	1.63	28.66	37.49	0.12	1.26	0.79	Marine
		BMD05	1.09	9.28	60.46	0.40	0.69	1.67	Terrestrial
		CAN06	4.13	30.47	51.91	0.31	0.70	0.46	Terrestrial
		CAN07	5.08	13.59	65.30	0.55	0.60	0.54	Terrestrial
		CAN08	3.97	30.90	47.18	0.30	0.67	0.52	?Mixed
Kutei		KTM01	11.22	n.d	n.d	n.d	n.d	0.71	Terrestrial
		KTM02	10.35	n.d	n.d	0.83	n.d	0.49	? Terrestrial
		KTM03	6.08	n.d	n.d	0.81	0.72	0.78	Terrestrial
Niger Delta Basin	North-East	NDE01	2.87	30.23	43.65	1.33	0.66	0.96	Terrestrial
		NDE02	2.78	28.34	44.84	1.60	0.68	0.81	Terrestrial
		NDE03	3.01	27.57	45.49	1.88	0.74	0.92	Terrestrial
		NDE04	2.69	30.70	39.23	1.19	0.73	0.82	? Terrestrial
		NDE05	3.79	26.82	49.16	1.74	0.71	0.75	Terrestrial
		NDE06	2.71	30.92	39.85	1.16	0.61	0.87	? Terrestrial
		NDE07	2.74	30.69	40.34	1.53	0.77	0.75	Terrestrial
		NDE08	4.29	22.45	57.19	2.05	0.63	0.89	Terrestrial
	North-West	NDW09	2.09	33.16	38.96	0.50	1.17	0.81	Mixed
		NDW10	1.91	31.89	37.77	0.42	0.99	0.77	Mixed
		NDW11	1.75	32.35	35.89	0.45	1.10	0.88	Mixed
		NDW12	2.71	25.58	44.82	1.23	0.81	1.06	Terrestrial
		NDW13	2.16	31.40	42.23	0.71	0.93	0.96	Mixed
		NDW14	1.77	31.39	42.10	0.72	0.90	0.95	?Mixed
		NDW15	2.53	26.65	46.00	1.54	1.04	0.87	Terrestrial
	Central	NDC16	3.20	29.96	42.05	1.01	0.83	0.90	? Terrestrial
		NDC17	3.87	30.14	35.49	0.98	0.70	1.11	?Mixed
Reference oils		TRO01	1.59	34.36	33.17	0.17	0.83	1.14	Mixed
		NSA02	1.01	32.12	36.96	0.11	1.36	0.72	Mixed
		NSA03	1.35	63.66	20.16	0.06	2.37	0.84	Marine
		NSA04	1.29	67.66	15.55	0.00	2.27	0.62	Marine
		NSV05	1.53	59.59	21.42	0.00	1.72	0.71	Marine

Source rock depositional environments have been deduced using plots of molecular characteristics such as Pr/Ph ratios, gammacerane index and the Pr/*n*- C_{17} vs. Ph/*n*- C_{18} plots (Figure 4.7; Figure 4.16; Figure 4.17). In general the source rock depositional conditions correspond with the source rock organic matter type interpreted from sterane and terpane molecular data. Source rock anoxia was also inferred from a histogram plot of the pristane/phytane ratios of all the oils in the sample set (Figure 4.16). The Beaufort-

Mackenzie Delta oils are split into two groups of oils whose source rocks are deposited over wide-ranging conditions, from anoxic to oxic environments. Similarly, the Niger Delta oils, by this plot, are clearly expelled by source rocks laid in dysoxic to oxic depositional environment. Some Niger Delta and Beaufort-Mackenzie oils show high marine algae biomarker source signatures, characteristic of source rock deposition in less oxygenated conditions. This is evidenced by their low Pr/Ph ratios (<2.5) and presence of gammacerane (up to 0.17, Table 4.1and Table 4.3). Other biomarker indicators of high marine algae inputs include high C_{27}-diasteranes, C_{30} (4-methyl-24-ethyl)-steranes (not observed in study samples), high C_{29}-sterane/C_{30}-hopane (>1.5), and DBT/Phen ratios (>1). However a few Beaufort-Mackenzie oils show exceptions, with insignificant amounts of gammacerane. There are not enough samples to make this inference for the source rocks of the Kutei oils but other attributes of these samples, e.g. very high Pr/Ph ratios (>6, Table 4.6) and lack of gammacerane, are suggestive of deposition under more oxic conditions, devoid of water column stratifications (Curiale *et al.*, 2005).

Another means of making inferences on the oils source rock depositional environments and lithology is the established relationship between the ratios of dibenzothiophene/phenanthrene (DBT/P) and pristane/phytane (Pr/Ph) as shown in Figure 4.18 (Hughes *et al.*, 1995). All three Kutei oils were grouped in the 4th (mostly associated with fluvial/deltaic environments) section of the chart. However, oils from the Beaufort-Mackenzie Delta, as observed earlier, are classed into two main groups (3 and 4) as well as a possible third group (2), occupied only by BMD01 and characterised as less oxygenated, sulphate-poor lacustrine shale. Groups 3 (BMD03, BMD04, BMD05), and Group 4 (BMD02, CAN06, CAN07, and CAN08) are characterised by less oxygenated marine shale and more oxic fluvio/deltaic carbonaceous coal environments (Hughes *et al.*, 1995). One of the three Beaufort-Mackenzie oils plotting in Group 3, (BMD05; Table 4.6) possesses a terrigenous biomarker signature (e.g. high %C_{29}) while the other two are dominated by high marine algae biomarker source signature. On the other hand, oils from the Niger Delta are more widely distributed on this plot. They are still, however, grouped according to these divisions. Similar to the Beaufort-Mackenzie oil grouping, they are classed into Group 3 or 4. Most oils of North-Eastern and Central sections of the delta constitute the bulk of the oils plotting in Group 4 (Figure 4.18) owing to an overwhelmingly terrigenous bacterial organic matter received by their sources. However, a majority of the Niger Delta oils cluster around the boundary between Groups 3 and Group 4. These groupings are as expected for the case study (Tertiary) oils when compared with the position of the reference (marine) oils on the

plot. The reference oils (North Sea including the mixed marine/terrestrial TRO01) plotted within Group 3 (marine/mixed shale) but closer to the Group 2/3 boundary.

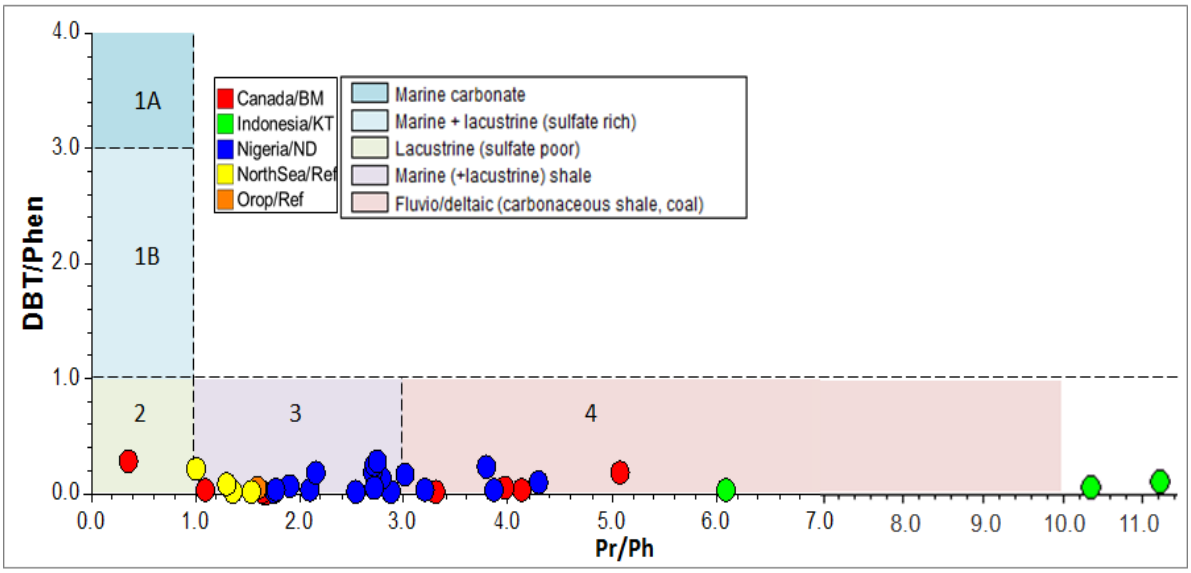


Figure 4.18 Plot of dibenzothiophene/Phenanthrene (DBT/P) versus pristane/phytane ratios for the studied oils. The key to the coloured zones/boundaries (after Hughes *et al.*, 1995) allows inference on oil source depositional environment and lithology. Exceptions to these zones are common, hence boundaries are adaptable.

The relationship plot between the DBT/P and Pr/Ph ratios (Figure 4.18) characterises oils into various source rock depositional environment/lithology groups namely: marine carbonate, marine + lacustrine (mixed sulphate-rich), sulphate-poor lacustrine shale, mixed marine/lacustrine shale and fluvio-deltaic carbonaceous shale/coal. Although the more soluble DBT can be depleted by water washing, (e.g. Lafargue and Barker, 1988), the DBT/P ratio remains an excellent solo indicator of source rock lithology with values >1 for carbonates and <1 for shales. In this study, computed DBT/P values (0.01-0.27, Table 4.4) for all samples indicate a non-carbonate source rock for all of these oils. Figure 4.18, therefore, provides a means of assessing the source rock depositional conditions as well as the source rock lithology of these oils. In conclusion, these oils have been generated from either marine shale, mixed (marine/lacustrine) shale or deltaic carbonaceous shales or coals.

4.4.2. *Source Rock Kerogen-Type*

The type of major organic matter input (i.e. algae vs. terrigenous higher plants) to petroleum source rocks is often interpreted based on their sterane and angiosperm marker (oleanane) compositions. Oleanane appears to be present at variable concentrations in all analysed Tertiary deltaic oils. The relative abundance of one or more of the C_{27}-C_{29} steranes in a crude oil is a reflection of the sterane composition of the type of source rock kerogen from which such oil was expelled upon maturation. Briefly, high relative abundances of the C_{27} and C_{29}-

steranes are derived from marine phytoplankton and algae, and terrigenous higher plants and bacteria, respectively (Seifert *et al.*, 1979, Peters and Moldowan, 1993). A ternary plot of C_{27}-C_{29} sterane composition of oils from the case study basins and the reference samples (Figure 4.3) has been used as additional tool for relating the oils to their source rock organic matter makeup.

The oils of the Beaufort-Mackenzie Delta again separate into two main groups (Figure 4.3). The group plotting close to the C_{29} sterane apex implies terrigenous higher plant organic matter source for these oils while the other group of oils plotting in the higher C_{27}-sterane region can be said to originate from predominantly marine source rocks with high algal input. Similar observations about two types of oils occurring within the Tertiary deltaic reservoir in Beaufort-Mackenzie Delta have been documented by previous workers (e.g. Brooks, 1986a, Curiale, 1991). It is thought that these 'marine' oils are sourced within the Late Cretaceous sequences (below the Tertiary delta) but the oils have migrated into upper sequences and are now reservoired within the Tertiary sands of the delta.

Likewise, the oil samples from the Niger Delta are classed into two end-member groups and possibly, an intermediate group based on Figure 4.19 and Figure 4.3. The high inputs of terrigenous organic matter to the source units of most North-Eastern, central, and some of the North-Western oils of the delta (B and C, Figure 4.19), is an indication of accumulations resulting from various zones within the delta. Most North-Western oils have mixed marine and terrigenous organic matter source signatures (A, Figure 4.19) which reflect one of mixed accumulations and generation from source rocks that are deposited away from the delta (Pro-delta shales; Samuel *et al.*, 2009), with copious marine algae and terrigenous organic matter inputs. The Kutei oils, as shown on the Pr/*n*- C_{17} vs. Ph/*n*- C_{18} plot (Zone I/II; Figure 4.17), clearly possess characteristics of intra-delta derived oils from coaly shales with abundant angiosperm input.

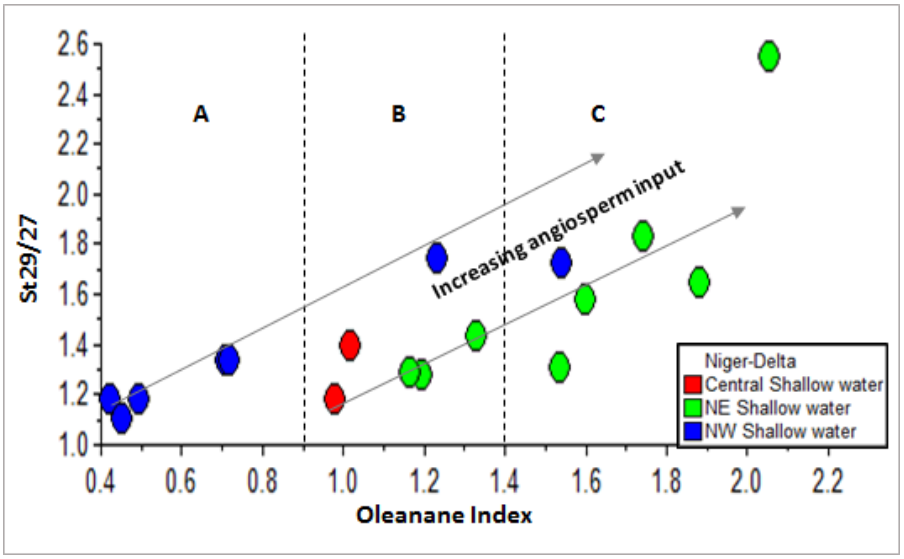


Figure 4.19 Cross-plot of the 5α(H),14α(H),17α(H)-20*R*-C_{29}-sterane/ 5α(H),14α(H),17α(H)-20*R*-C_{27}-sterane ratio vs. oleanane/αβ-C_{30}-hopane ratios (oleanane index) for the oils of the Niger Delta. Axes values are measured from peak areas in m/z 217 and 191 mass chromatograms respectively and listed in Table 4.2 and Table 4.3. (after Curiale *et al.*, 2000). Note the 3 oil groupings (A-C) correspond to relative amounts of terrestrial organic matter input to their sources.

4.5.Thermal Maturity and Alteration

This study is focussed on the possibility that the case study Tertiary deltaic oils might have come into contact with, and dissolved thermally immature molecular marker components along its migration pathway. It is therefore important that the thermal maturity of these oils be well-assessed using an appropriate set of parameters.

4.5.1. *Assessment Parameters*

While many of the study samples are believed to be have been generated from a common source (e.g. Niger Delta oils), few others are characterised as biodegraded. There is, therefore, the need for precise maturation assessment using indicators that are independent of organic matter type and less susceptible to biodegradation. One of such specific ratios, the Methylphenanthrene Index (MPI-1), correlates strongly with measured (microscopic) mean vitrinite reflectance (R_o) regardless of burial history, and is defined as:

$$MPI = 1.5 \times ((2MP + 3MP)/(P + IMP + 9MP))$$

Equation 4.1 Expression for the Methylphenanthrene Index (MPI-1).

Where: P, 2MP, 3MP, IMP and 9MP are the concentrations of phenanthrene and 2-, 3-, 1- and 9-methylphenanthrenes respectively (Radke *et al.*, 1982).

MPI-1 has been used to derive calculated vitrinite reflectance (R_c) using a working relationship for 0.65% < R_o< 1.35% (R_c = 0.6 MPI-1 + 0.4), and for R_o > 1.35% (R_c = -0.6 MPI-I + 2.3); R_c values for all crude oil samples are represented within the aromatic biomarker parameter data (Table 4.4). Based on the classification of crude oil maturity by R_c values as either immature (0.7- 0.8%), mature (0.8- 0.9%), post-mature (0.9-1.0%) or over-mature (1.4 - 2%) (Radke, 1988b), many of the samples can be classed as mature while few others can be said to be post-mature. All Niger Delta oils are mature with values (0.85-1.04%) belonging to Type II/III oils (R_c ~0.85%). The oils of the Beaufort-Mackenzie Delta exhibit varying maturity levels (0.68-1.40%). BMD05 (1.40%), by this classification, is overmature, and is very likely a condensate sample (cf. Curiale, 1991). But for KTM02 (R_c = 0.69), the thermal maturity of the biomarker-lean Kutei samples are supported by these values (R_c ≥0.80%). The reference samples (excluding TRO01) show R_c values around 0.85% (0.77-0.90%), indicating oil window maturity (cf. Peters *et al.*, 2005).

A number of the field samples show maturities about the peak oil window (R_o<1.35%; R_c=0.7-1.40%), hence some of the more reliable biomarker parameters such as diasterane/sterane, hopane/sterane, moretane/17α-hopane, and C_{27}-trisnorhopane (T_S / T_m or T_S/[T_S + T_m]) ratios, are still useful for assessing maturities in this range, as observed in these oils. Other useful parameters such the C_{29}αα-sterane and C_{32}αβ-hopane isomerization ratios, are of limited or no use at these levels of maturity.

4.5.2. *Sterane Maturity Ratios*

Figure 4.16, Figure 4.17 and Figure 4.20 are plots of applicable thermal maturity biomarker ratios. Wide ranging measured values for the 5α(H), 14α(H), 17α(H)-C_{29}-20(*S*/*S*+*R*) sterane maturity parameter (Table 4.2) are exhibited by the Beaufort-Mackenzie (0.2-0.55) and Niger Delta (0.33-0.59) oils, as well as for the C_{29}-20*S*+*R*(αββ/αββ+ααα) ratios, 0.27-1.00 and 0.35-0.44, respectively (Table 4.2). However, majority of the study oils tend to have values around 0.5-0.6 for the C_{29}-αα20*S*/(20*S*+20*R*) maturity parameter which is near their equilibrium value prior to early oil window maturity (Peters and Moldowan, 1993). A plot of the relationship between both sterane maturity parameters (Figure 4.20) is a reflection of the oils' different thermal maturity levels due to different timing of oil generation and expulsion from their source rocks assuming the oils biomarker signature remained unaltered either during migration or in-reservoir. High values suggest oil may be more thermally advanced than its expulsion temperature. These values, according to Seifert and Moldowan

(1981), may attain equilibrium of ~0.55 and 0.60-0.70 respectively with increasing thermal stress (Figure 4.20). The indistinct correlation between the C_{29}-ααα(20*S*/[20*S*+20*R*]) and C_{29}-(αββ/[αββ+ααα])-sterane ratios (Figure 4.20) as observed amongst the Niger Delta oils suggests that their variation is not related to thermal maturity differences (Sonibare *et al.*, 2008); or that some of the samples have attained maturities just beyond peak oil window (R_0~0.9%) at which the isomerisation reactions (20*S*↔20*R*) have reached an endpoint (Peters *et al.*, 2005).

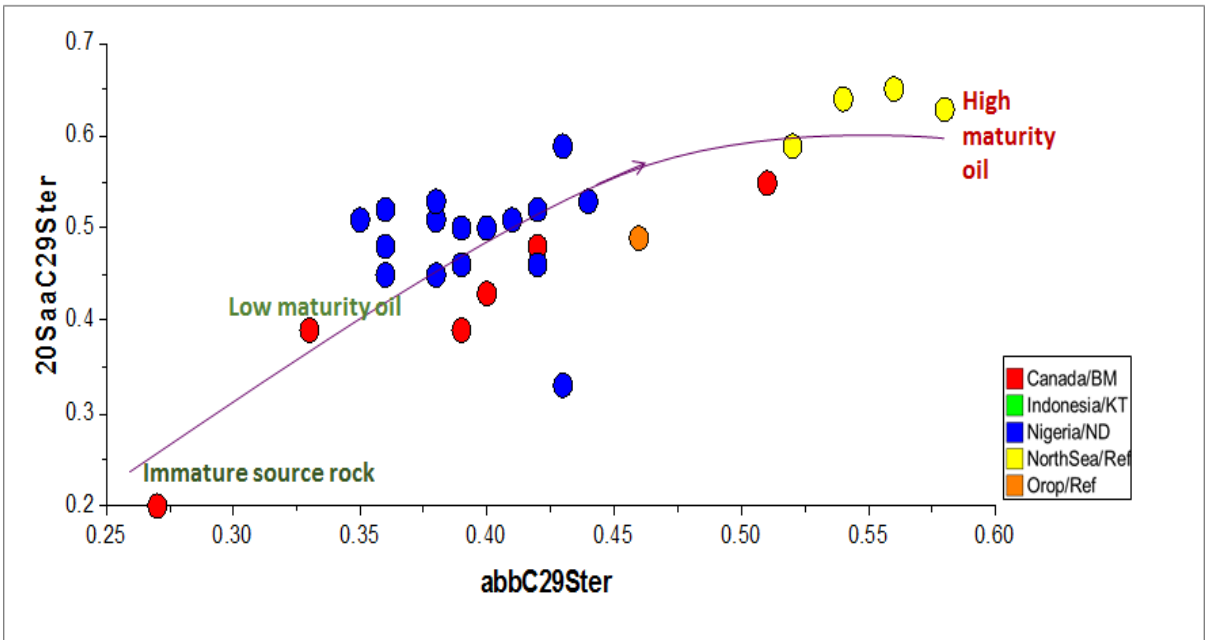


Figure 4.20 Plot of '20*S*aaC29Ster' (% St29S/R (% 5α(H),14α(H),17α(H)-C_{29} 20*S*/(20*S*+20*R*)) sterane isomerisation maturity versus 'abbC29Ster' (C_{29}-iso/regular (5α(H), 14β(H),17β(H)-20*S* +20*R*/ 5α(H),14α(H),17α(H)-20*S*+20*R*) steranes. Most of the Tertiary oils are shown to fall within the early mature to mature range. The equilibrium values (~0.55 and 0.60-0.70) for both parameters are also reflected in this plot. Note the distinction of the study samples from the North Sea reference samples which are shown to be of higher maturity.

4.5.3. *Terpane Maturity Parameters*

The homohopane isomerisation at C-22 is specific for early maturity assessment of crude oil and rock extract. Due to coeluting peaks which affected the C_{31} epimer ratio, in the case of biodegraded oils, C_{32}-αβ- bishomohopanes data were used to calculate this ratio for the oil samples. Calculated 22*S*/(22*S*+22*R*) ratios ranged from 0.51 to 0.61 for the case study oils, and 0.56 to 0.60 for the reference oils (Table 4.3). Because this ratio has been shown to increase from nil to equilibrium value (~0.6) during maturation (Seifert and Moldowan, 1979), the values suggest that most of the samples have reached the main phase of oil generation. This data correlates well with derived R_c values for R_o<1.35% as shown in Figure 4.21. Furthermore, the absence of the biological 17β(H), 21β(H) homohopanes in all the

studied oils is a confirmation of the thermal maturity of these oils (e.g. Seifert and Moldowan, 1979).

The moretanes/hopanes maturity parameter is highly specific for assessment of immature to early mature oils (Peters *et al.*, 2005). Measured using either of C_{29} and C_{30} homologs, its applicability is based on the less thermally stable 17β-moretanes which decrease in abundance relative to their 17α-hopane counterparts with increasing maturity. Data shown in Table 4.3 for all studied oils have, from their low values (minimum of 0.13), again characterised these samples as mature oils. Based on these results (0.16-0.27 for the Canadian samples; 0.17-24 for the Nigerian oils and 0.13-0.20 for the reference oils), the Tertiary sourced case study oils tend to show higher ratios, (mostly between 0.16 and 0.27) than those of the older sourced reference oils (NSA03, NSA04, and NSV05).

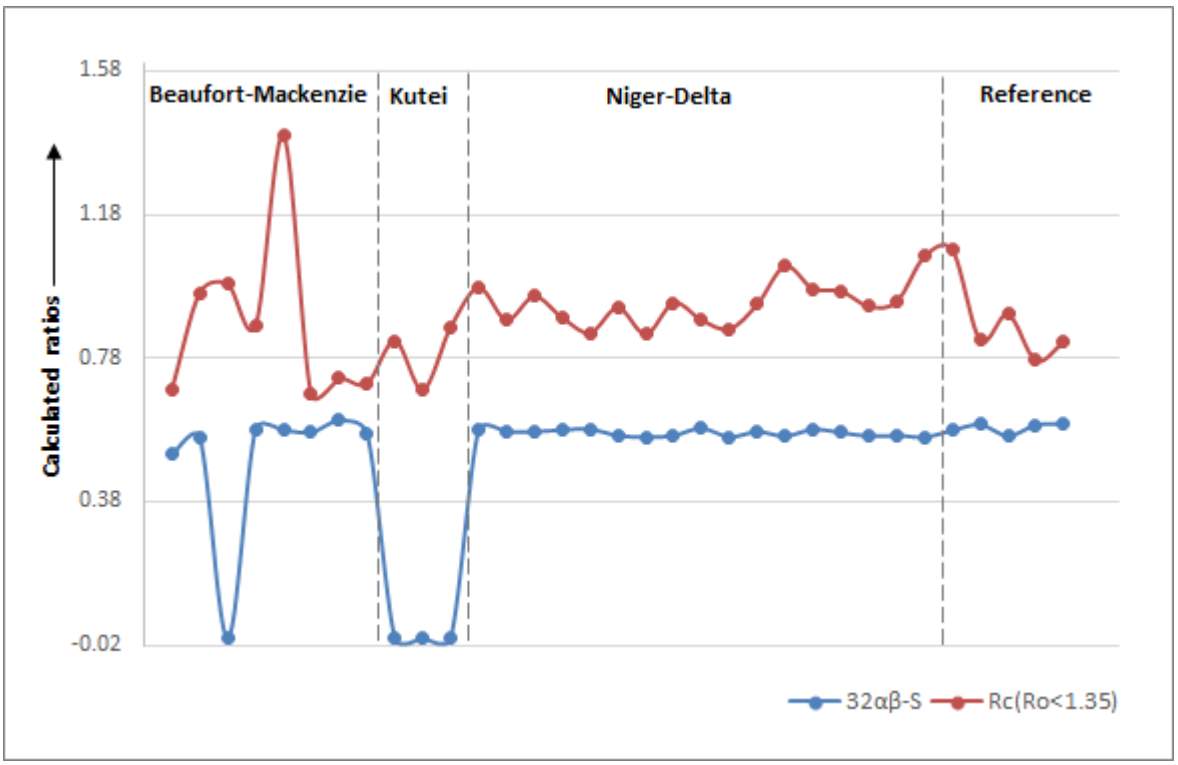


Figure 4.21 Scatter plot showing the correlation between the C_{32} epimer ratios and calculated vitrinite reflectance for R_o<1.35%.

The 22, 29, 30-trisnorneohopane/22, 29, 30-trisnorhopane (T_s/T_m) ratio is known to increase rapidly at high maturities (Peters and Moldowan, 1991), and its applicability over a wide range of maturity (immature to postmature) is based on relative stability of these C_{27}-hopane isomers with maturation (Peters *et al.*, 2005). This parameter ranged in values from 0.45-1.26; ~0.72, 0.61-1.17; and 1.36-2.37 for the Beaufort-Mackenzie Delta, Kutei Basin, Niger Delta, and the reference 'marine' oils respectively. Being source-dependent, the C_{27} trisnorhopane is stated to be a reliable maturity indicator for oils from a common source with

consistent organic facies (Seifert and Moldowan, 1978). Hence, the variations seen in these similar sets of oil could be evidence of varied sources as well as maturities.

4.5.4. *Biomarker Parameter Relationships*

An attempt is also made at establishing a relationship between selected thermal maturity parameters for the oils in the study set. Although the measurable values of these parameters for the oils indicate at least, a mid-mature oil window for most of these oils, there seem to be a vague correlation between displayed maturity parameters across samples. This could mean that the oils were expelled from their source rocks at variable thermal maturities. Because, unlike the saturate markers, higher concentrations of the key alkyl-aromatic compounds are shown to persist at elevated maturation beyond 0.9% R_o levels, aromatic maturity parameters are considered more versatile maturity assessment tools where indicators based on common biological markers are of questionable significance. Such instances were seen in the BMD03, and the Kutei samples, which are characterised by reduced biomarker (esp. cyclic) concentrations; and although they do not appear to be overly mature, the unusual absence of cyclic biomarkers is typically associated with condensates (as these samples are classed), or increased maturity, extending into the post mature zone. However, a general distinction of the highly mature reference oils from their case study counterpart, most of which are mid- to late mature, is demonstrated (e.g. Figure 4.20). Again, these parameters are more correlated across Niger Delta oils than in the other oils.

The dimethylnaphthalene ratios (DNR-1 and DNR-2) and methylphenanthrene indices (MPI-1and MPI-2) which are derived from aromatic hydrocarbon data from all analysed oils (Table 4.4) are also very frequently applied maturity parameters. Cross plots of both ratio pairs: DNR-2 vs DNR-1 and MPI-2 vs MPI-1, are shown in Figure 4.11 (a, and b). These graphs generally suggest some degree of positive correlation between parameters, but the MPI-2 vs MPI-1 relationship (Figure 4.11b) shows a very good correlation, with a clear increasing maturity trend (e.g. Sonibare *et al.*, 2008).

Similarly a scatterplot of the pristane to *n*-heptadecane (Pr/*n*-C_{17}) and phytane to *n*-octadecane (Ph/*n*-C_{18}) ratios (Figure 4.17) which are occasionally applied in correlation studies, in terms of source rock depositional conditions and organic matter type, can often be used to approximate the level of thermal maturity of oils, though biodegradation as well as thermal maturity can affect both ratios (Leythaeuser and Schwarzkopf, 1986). The study samples are generally regarded as non-biodegraded oils; however, severe biodegradation

were observed in few of these samples (BMD01, BMD02, CAN07, CAN08, NDW11) while BMD04 and NDW14 are slightly biodegraded (GC fingerprints; Appendix III-c). These oils are shown to plot close to, or within the 'immature and/or biodegraded' region as shown in Figure 4.17. Maturity parameters such as high T_s/T_m and low moretane/hopane ratio values indicate the relatively high maturities of these oils.

4.6. Characterisation of the Crude Oils using Rare Compounds

One of the main objectives of this study (c.f. Chapter 1; Section 1.6) was to isolate, characterize and use the concentrations and distributions of selected 'unusual' components of various Tertiary deltaic oils to infer migration-contamination, where perceived, in these oils. These 'rare' compounds are the unsaturated hydrocarbons (olefins) and non-hydrocarbon carboxylic acids. Their unusual occurrence in certain crude oils has been proposed as a consequence of one or more migration alteration processes (e.g. Jaffé *et al.*, 1988a, Curiale, 2002). Based on the geological settings of the petroleum systems in place at the time of oil generation, expulsion, migration and accumulation, 'contamination' of migrating oil by these compounds have been previously proposed to occur in Tertiary deltaic petroleum systems (Jaffé *et al.*, 1988b, Jaffé and Gallardo, 1993, Curiale, 1995, Curiale and Bromley, 1996b, Curiale and Frolov, 1998, Curiale, 2002).

The results of the analysis showed that these compounds all occur in varying concentrations in most of the Tertiary-reservoired oils of Beaufort-Mackenzie, Niger Delta and Kutei Basin. Their relative abundance and overall distributions are suggestive of similar sources, containing terrigenous higher plant, specifically angiosperm input. These quantitative data and parameters, including routine specific markers such as oleanane and common biomarker ratios in these oils are reported below.

4.7. Unsaturated Hydrocarbons (UHC) - Olefins

Thirty three crude oil samples (including reference oils) were examined. Twenty eight of these were sampled from three well-known Tertiary deltaic petroleum provinces. It is assumed that secondary recovery methods had not been applied in the production of these oils. Such methods include natural gas injection, water-flooding, and the use of synthetic oil-based drilling fluids. If used in oil production, they could alter the composition of the petroleum by raising the concentration of particular components. The type of recovery method or drilling/testing fluids and/or additives employed in oil production could be a significant factor for consideration in the selection of study samples for migration study.

This is because drilling fluids used in some Deepwater and onshore operations could contain additives that impact fluid geochemistry and alter its composition. For instance, synthetic oil used as a type of base in oil-based muds contain significant amounts of olefins and esters which could undermine geochemical evaluation of migration effects based on increased olefin abundance in the 'contaminated' oils (e.g. Wenger *et al.*, 2004, Reddy *et al.*, 2007). In this case, a sample with unusually high amounts of olefins and/or carboxylic acids may lead to misinterpretation or wrong inference of migration-contamination, unless the effects of such recovery methods are first ruled out. No information, however, was given on whether secondary recovery methods were used for the oil samples in this study. Therefore the application of derived data is based on the assumption of secondary recovery free production which may limit the extent to which an inference is made on observed migration effects which may, in turn, affect the interpretation of the study findings.

Olefin isolation was carried out principally by TLC procedures described previously in Chapter 3. Olefins were detected in nearly all the oils investigated. The results of olefin analyses and quantifications are summarised in Table 4.7. Summed concentrations of measured olefins in the crudes ranged from trace amounts (<5 ppm) up to ~330 ppm. Although the concentrations are generally low in these oils, these results indicate that olefins are not as rare in crude oils as earlier acknowledged (Curiale and Frolov, 1998). Since low olefin content occurs frequently in theses samples, it would be expected that low olefin-containing petroleums will be widespread in the study, and other similar, basins. Identified classes of olefins, as shown in Figure 4.22, include *n*-alkenes (C_{12}-C_{26}), hopenes, diasterenes and oleanenes.

The gas chromatograms of whole UHC fractions of representative samples from each case study basin are shown in Figure 4.23. The olefin data of the reference oils are also represented (greyed) in Table 4.7. These samples contain some or all of the observed olefin groups. It was unexpected for these oils (except TRO01 and NSA02) to contain detectable amounts of olefins since, to the author's knowledge, no reports of olefin occurrence in marine oils of this nature had been documented. The 'abnormally' high concentration of olefin on the NSA02 is not understood, but geochemical characteristics of this sample showed that it is heavily biodegraded, and the highly viscous nature of the fluid at room temperature suggests that the oil may have undergone secondary or enhanced recovery methods whose processes altered the fluid composition by contaminants (olefins and acids,

in this case). However, the total olefin content of the reference oils are still lower than many of the case study Tertiary oils that contain considerable amounts (>20ppm).

Table 4.7 Whole olefin concentration data for identified classes of linear and cyclic olefins in the study samples.

SampleID	n-alkenes	Hop-17,21-enes	Oleanenes	Diasterenes	Me-diasterenes	Total olefins
	Amount (ppb)					(ppm)
BMD01	307	1982	n.d	29657	2591	35
BMD02	1069	1316	1462	40845	2357	48
BMD03	1040	n.d	n.d	54	8	3
BMD04	1786	304	350	8037	718	11
BMD05	900	3069	1647	26800	1817	34
CAN06	7104	5554	42621	124466	9967	190
CAN07	14513	526	7800	22798	1115	47
CAN08	2340	13618	64533	231750	18443	331
KTM01	3812	11	96	420	38	5
KTM02	4188	110	958	2554	258	8
KTM03	304	40	287	2062	114	3
NDE01	401	2417	4243	4258	552	13
NDE02	17292	964	16267	899	n.d	35
NDE03	7218	693	26777	1239	170	36
NDE04	5819	n.d	4004	n.d	n.d	10
NDE05	17065	242	10690	1209	168	30
NDE06	32433	191	43163	1294	n.d	77
NDE07	18634	446	24334	904	n.d	45
NDE08	482	5099	7083	3516	458	18
NDW09	11966	n.d	1200	n.d	n.d	14
NDW10	7010	52	747	137	n.d	8
NDW11	468	1760	4112	2516	308	9
NDW12	5395	7435	32445	13972	1764	61
NDW13	16112	4129	47699	6718	1031	78
NDW14	36429	1084	39892	962	390	83
NDW15	11007	154	8292	463	n.d	20
NDC16	56181	1332	8513	2064	214	69
NDC17	26355	7045	14975	9543	1132	59
TRO01	4863	6183	4071	8729	1359	25
NSA02	1382575	5744	554	44646	13850	1447
NSA03	2515	n.d	n.d	4678	1055	8
NSA04	792	n.d	n.d	575	128	2
NSV05	1635	296	n.d	5604	1084	9

n-alkenes = sum of all identified normal olefins (C_{12}-C_{27}); Hop-17(21)-enes is the sum of all identified C_{30}-C_{35} (22*S*+22*R*) Δ17,21-hopenes; Oleanenes = sum of 18α-olean-12-ene, olean-12-ene, olean-18-ene, olean-13(18)-ene and urs-12-ene, determined from peak area measurements on the m/z 218 mass chromatogram; Diasterenes = sum amount of all identified 10α and 10β-C_{27}-C_{29}- diaster-13(17)-enes [20*S*+20*R*]; Me-diasterenes = sum amount of all identified C_{28}-C_{30}-4β-methyl-10α-diasterenes (20*S*+20*R*); total olefins = total of summed concentrations of all olefins analysed in the study; n.m = not measurable; n.d = not detected due to absence or low concentration below detection limit.

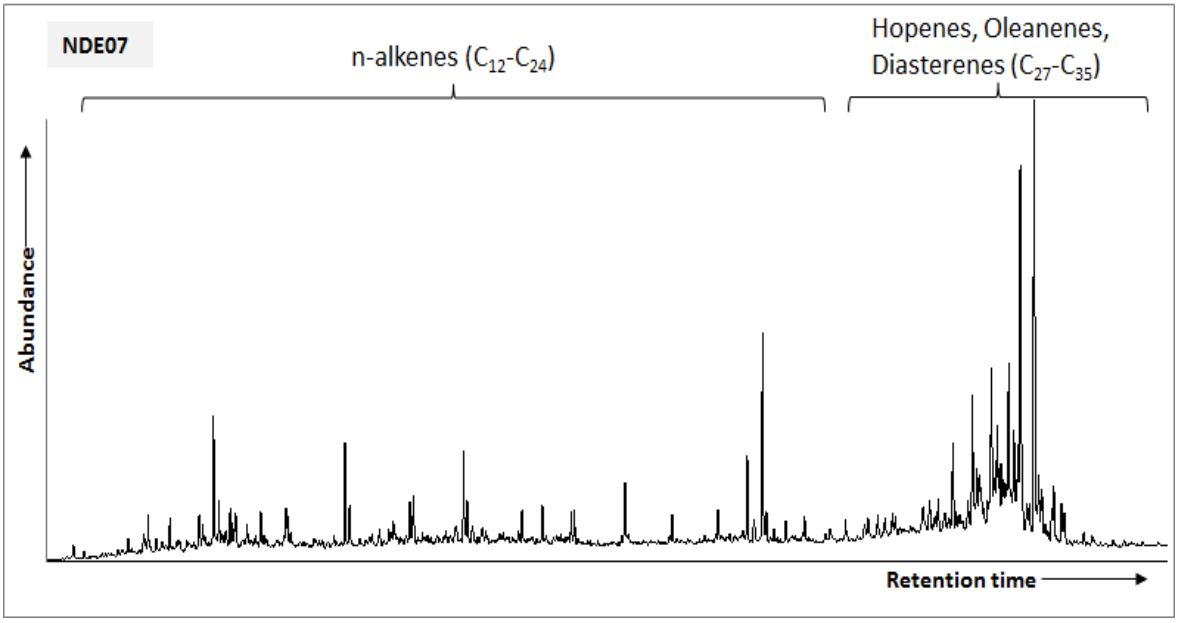


Figure 4.22 Representative total ion chromatogram (TIC) showing the distribution of olefins in a typical terrigenous oil (NDE07). The presence of *n*-alkenes, hop-17(21)-enes, oleanenes, diasterenes and methyl-diasterenes are revealed by extracted ion mass chromatograms (m/z 55, 397, 218, 257 and 271 respectively) of the isolated olefinic hydrocarbon fractions of the samples.

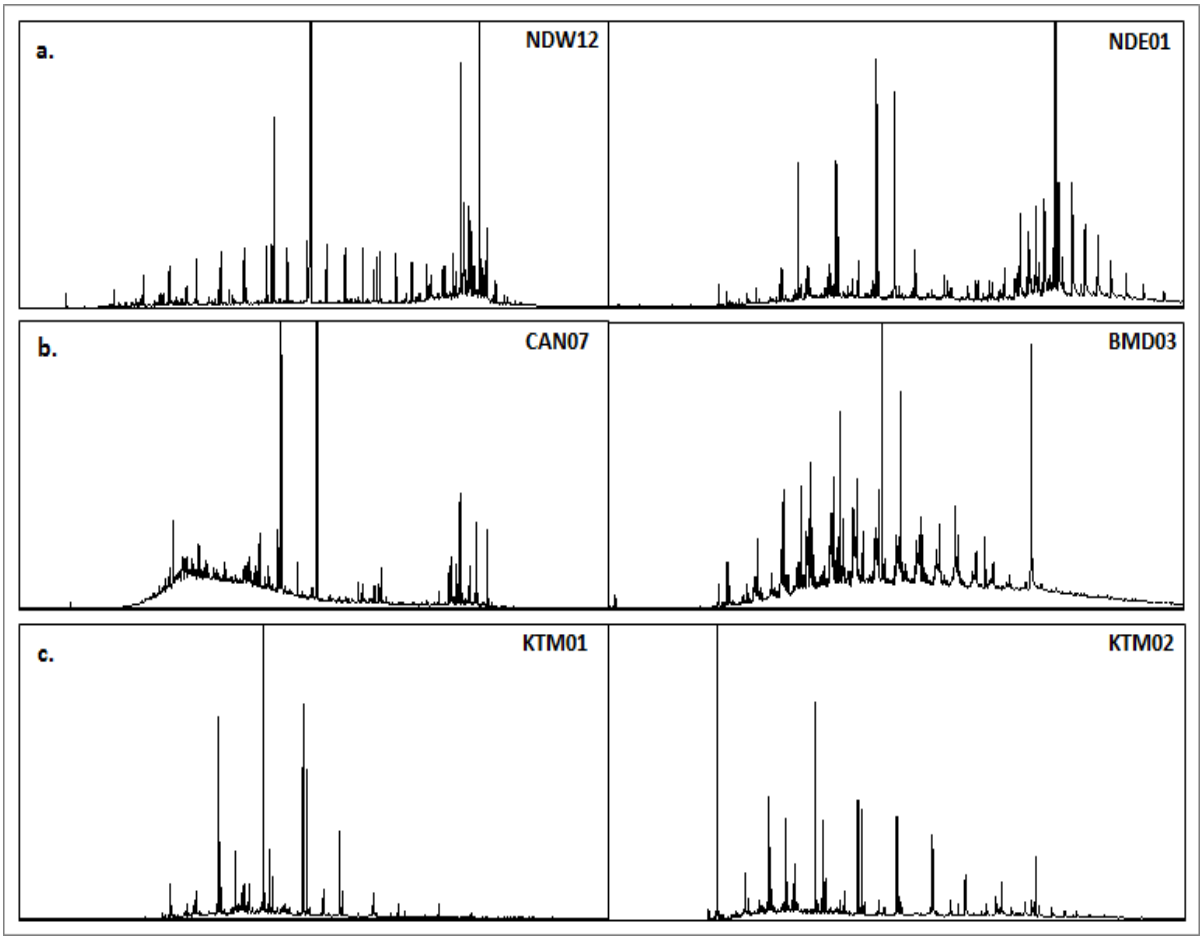


Figure 4.23 Gas chromatograms of the total olefin fractions isolated from aliphatic hydrocarbon fractions of two representative crude oils from each of 3 basins (a, b, c) are indicated. Normal alkene peaks elute, just before their corresponding *n*-alkanes. The cyclic olefins elute near the end of separation and could be clearly seen as distinct peak clusters (NDE01, NDW12, and CANO7). Their identification is achieved with GC-MS analysis. Note the absence or low abundance of the high molecular weight olefins in BMD03 and KTM01.

4.7.1. *Normal Alkenes*

The acyclic, linear olefins were identified in the m/z 55 mass chromatograms of the olefin fractions, and are dominated here by the *n*-alkenes. Their concentrations in the oils are very low but measurable, and include a wide range of C_{12}-C_{26} homologues. Laboratory contamination sources of alkenes in the samples was checked for by running procedural blanks alongside all sample batches. The gas chromatograms of the blank samples did not indicate any significant contamination as these were not quantifiable as shown in a TIC of a representative blank UHC sample (Figure 4.24).

Only terminal (by double bond position) olefins, which eluted approximately 5-12 seconds before their *n*-alkane counterparts in the gas chromatograms, were observed. In order to ascertain the position of the double bonds in the detected *n*-alkenes, relative retention time analysis using standard mix solution of C_{14}, C_{16} and C_{18} terminal *n*-alkenes with a couple of samples was performed under same GC conditions. Overlaid GC traces of the test samples (Figure 4.25) showed that detected *n*-alkenes in the samples eluted at exactly the same retention time as their standard counterparts.

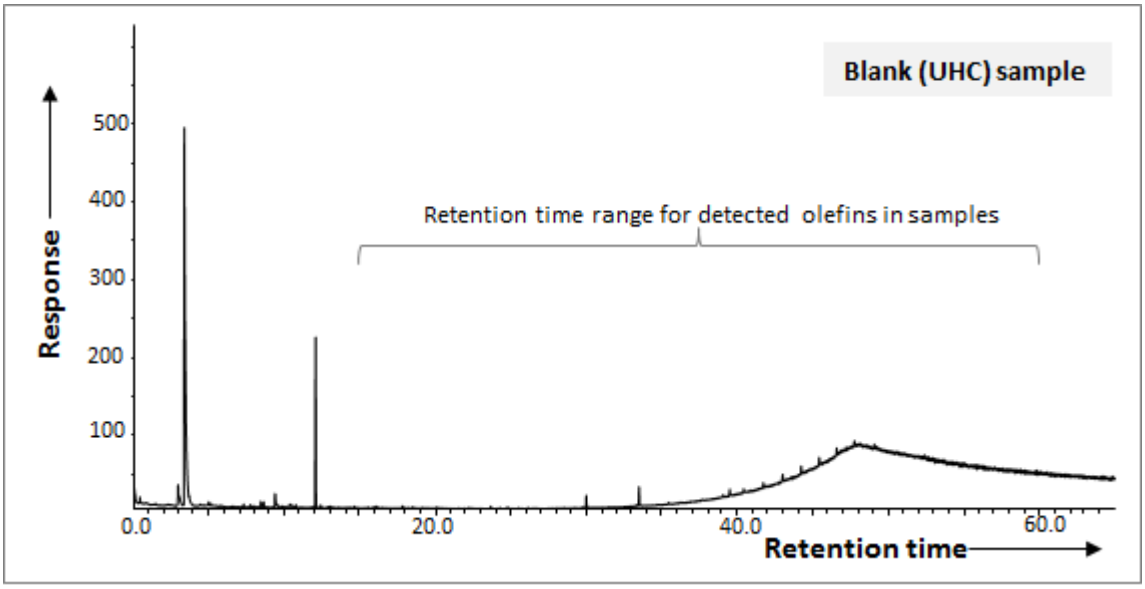


Figure 4.24 Total ion chromatogram (TIC) of a representative blank olefin fraction run as procedural blank with a batch of up to 8 sample fractions. Comparisons of significant peak areas in the blank and those of real samples revealed the blank peaks were a very low proportion of the lowest peaks in the olefin-containing oils.

Lower homologues (<C_{12}) of the *n*-alkenes were not detected (Figure 4.22; Figure 4.26; Table 4.7) and their carbon number profile are contrasting to those of their *n*-alkane (C_9-C_{36}) counterparts (Figure 4.27). The reference oils also contain considerable amounts of *n*-alkenes (~700-5000 ppb). However, besides NSA02 which has an unusually high amounts

of up to 1382 ppm, the *n*-alkene content of the reference samples are generally lower in concentration than those of many case study samples (up to 56000 ppb).

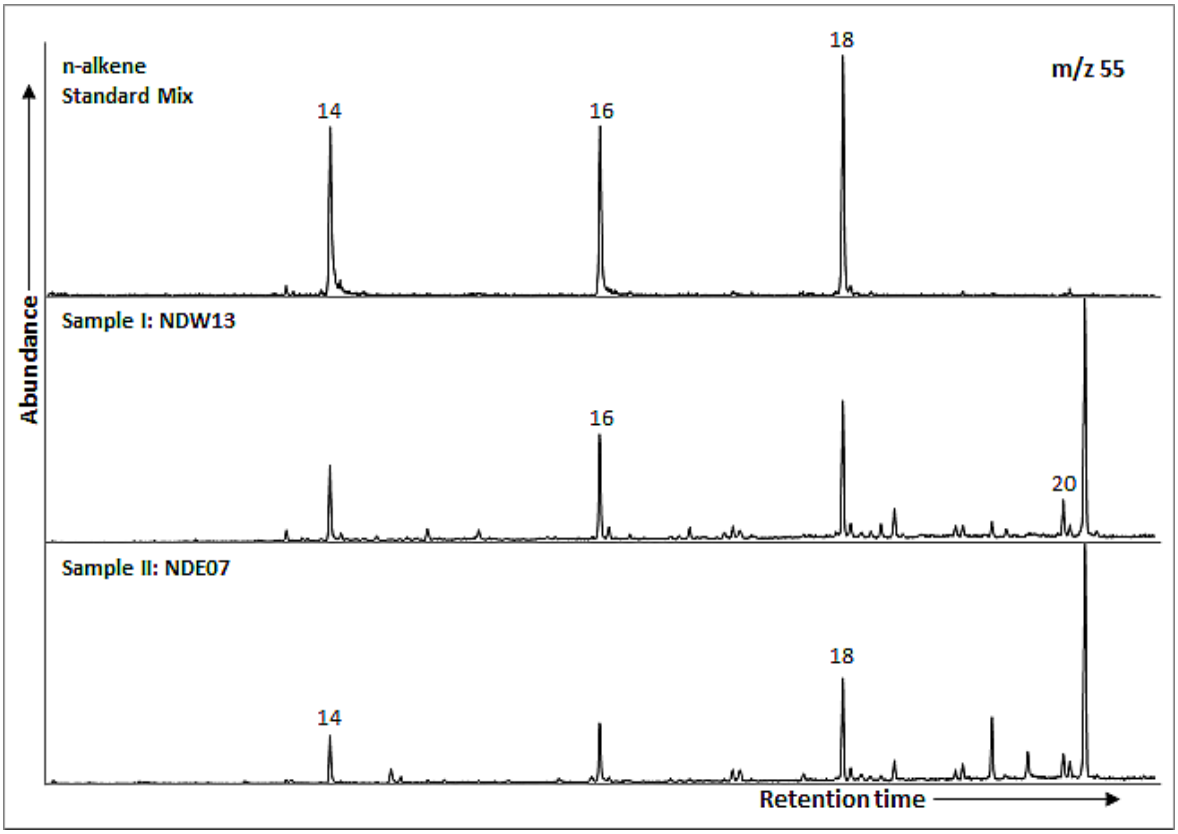


Figure 4.25 m/z 55 mass chromatograms showing the peaks identified as normal (terminal) alkenes based on their relative retention times. The top trace is of the pure standard solution (of C_{14}+C_{16}+C_{18} *n*-alkenes); the other two are those of the test samples, post-analysis. Only one well-resolved peak was observed for each carbon number homologue.

In addition, variations exist in the odd/even predominance (OEP) of both classes of straight-chain compounds. Figure 4.28 shows plots of OEP values versus *n*-carbon numbers of *n*-alkanes and *n*-alkenes for individual sample subsets, including the reference oils. While *n*-alkanes exhibit a typical odd predominance, as shown by values that plotted above unity (dashed lines in Figure 4.28), the *n*-alkenes with even carbon chain length (OEP<1; points below dashed lines) prevail, maximising mainly at C_{15} and C_{18} for *n*-alkanes and *n*-alkenes respectively. It is expected that normal alkenes found in crude should be linked to the same source as their accompanying alkane counterparts if the OEP or CPI values of both homologues are similar. However, the comparison of OEP data shown in Figure 4.28 suggests otherwise, and this could be a strong indication that the origin of the *n*-alkenes is different from that of the presumably source-derived *n*-alkanes.

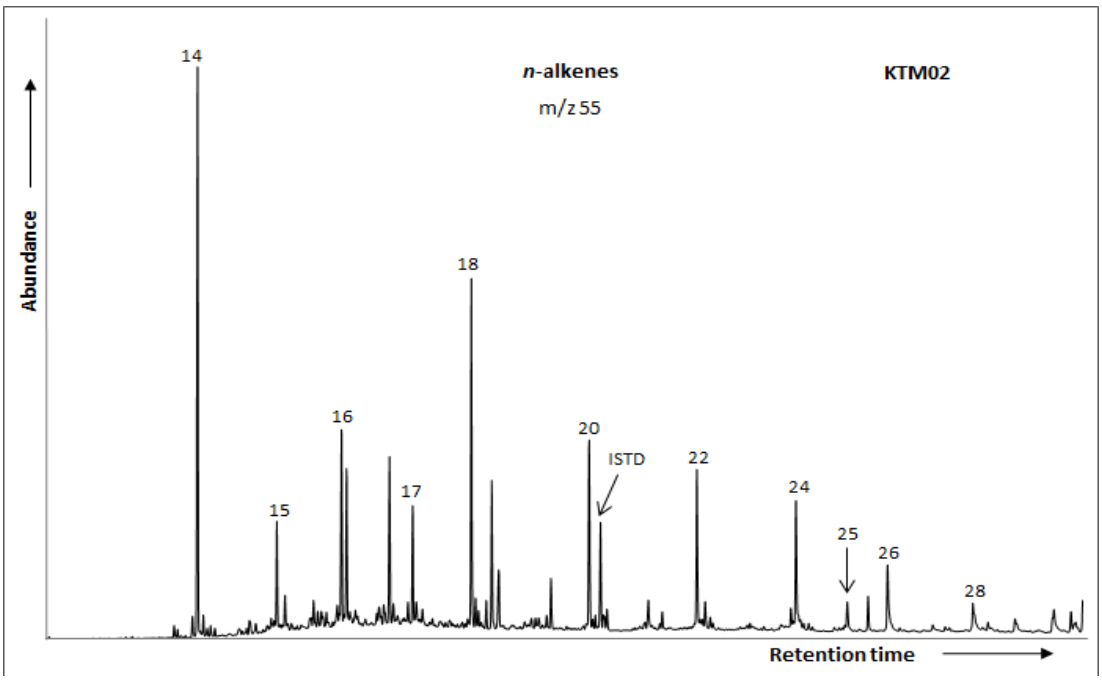


Figure 4.26 M/z 55 mass chromatogram of unsaturated hydrocarbon fraction of a representative Tertiary delta oil from the Kutei Basin. The numbers on the peaks denote the carbon chain length; ISTD = quantitation internal standard: Cis-2-Methyl-7-octadecene.

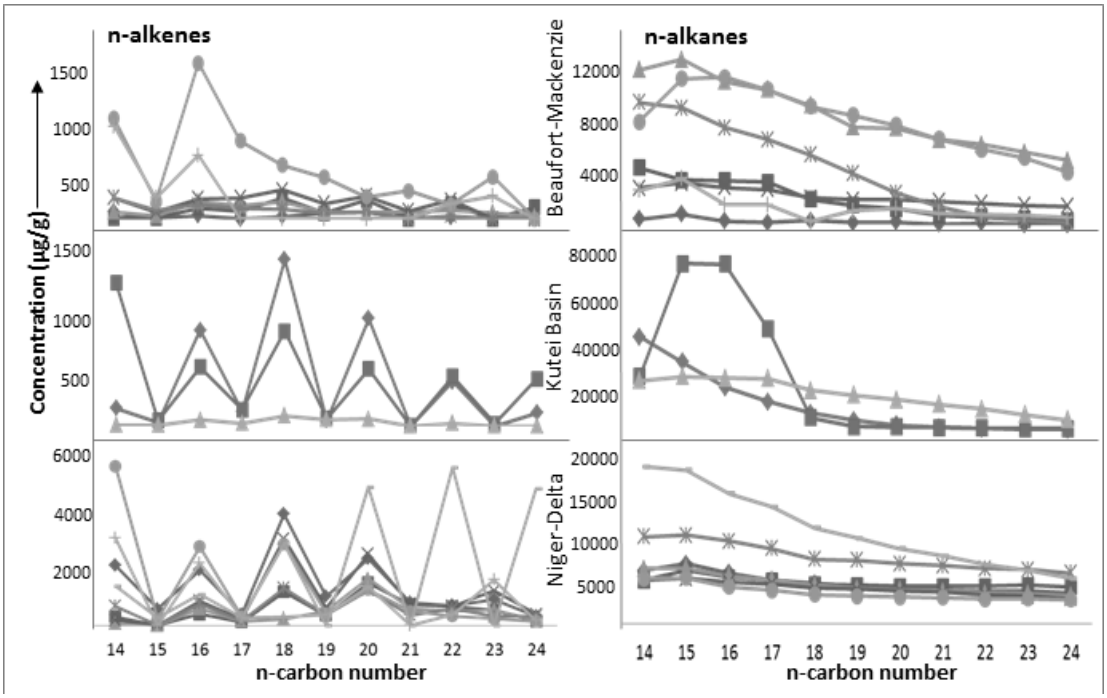
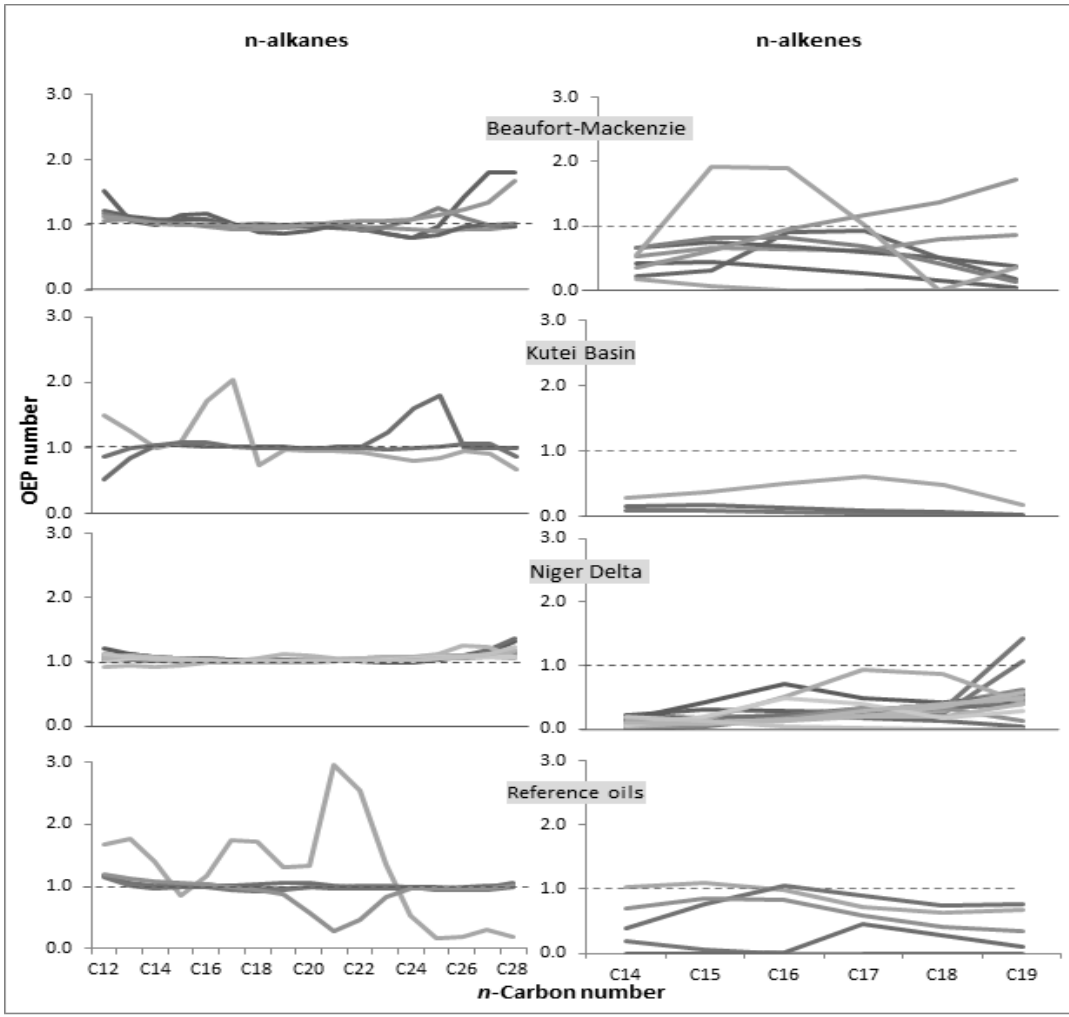


Figure 4.27 Line plots of carbon number (C_{14-24}) distribution of linear alkenes and alkanes in oils from each deltaic basin.

Similarly, comparison of the C-number distribution for both straight-chain series (Figure 4.27) showed a general indication of even carbon number preference for the *n*-alkenes, while the carbon preference in the alkanes is not directly obvious. These plots (Figure 4.27) reinforce the dissimilarity in the carbon profiles of this pair of compounds in the case study oils, which could be valuable in elucidating the source of accompanying normal alkenes in samples that contain them.



OEP Number for n-alkenes

Sample	C14	C15	C16	C17	C18	C19
BMD01	0.23	0.31	0.91	0.94	0.52	0.18
BMD02	0.42	0.44	0.36	0.28	0.16	0.04
BMD03	0.53	0.66	0.64	0.63	0.81	0.86
BMD04	0.66	0.76	0.68	0.60	0.51	0.38
BMD05	0.68	0.82	0.82	0.68	0.43	0.15
CAN06	0.35	0.63	0.96	1.17	1.38	1.73
CAN07	0.55	1.92	1.90	1.02	n.m	n.m
CAN08	0.18	0.08	n.m	n.m	n.m	0.37
KTM01	0.09	0.09	0.07	0.04	0.03	0.01
KTM02	0.15	0.18	0.14	0.10	0.06	0.02
KTM03	0.30	0.37	0.51	0.62	0.49	0.17
NDE01	0.22	0.31	0.29	0.27	0.34	0.46
NDE02	0.22	0.17	0.20	0.29	0.39	0.56
NDE03	0.12	0.17	0.21	0.28	0.40	0.61
NDE04	0.16	0.43	0.72	0.50	0.41	0.53
NDE05	n.m	0.05	0.17	0.28	0.23	1.07
NDE07	0.06	0.12	0.23	0.33	0.30	1.42
NDE08	0.08	0.16	0.19	0.18	0.12	0.04
NDW09	0.10	0.12	0.15	0.21	0.29	0.50
NDW10	0.10	0.17	0.22	0.28	0.32	0.39
NDW11	0.02	0.05	0.17	0.32	0.34	0.13
NDW12	0.17	0.16	0.50	0.95	0.87	0.42
NDW13	0.08	0.11	0.14	0.20	0.34	0.58
NDW14	0.05	0.10	0.14	0.19	0.20	0.39
NDW15	0.07	0.21	0.50	0.39	0.17	0.28
NDC16	0.10	0.07	0.14	0.28	0.39	0.50
NDC17	0.20	0.12	0.05	0.01	n.m	n.m
TRO01	0.19	0.06	n.m	n.m	n.m	n.m
NSA02	n.m	n.m	0.01	0.45	0.29	0.10
NSA03	1.04	1.10	0.98	0.73	0.63	0.69
NSA04	0.40	0.77	1.06	0.90	0.74	0.76
NSV05	0.69	0.86	0.82	0.58	0.41	0.35

$$OEP_{number} = \left[\frac{(C_i + 6C_{i+2} + C_{i+4})}{(4C_{i+1} + 4C_{i+3})}\right]^{(-1)^{i+1}}$$

Figure 4.28 Comparison of plots of odd/even predominance (OEP) numbers versus *n*-carbon numbers for normal alkanes and alkenes; the accompanying table shows calculated OEP numbers (for *n*-alkenes) used in the plots. The values are derived from an expression for carbon preference index (CPI) by Scalan and Smith (1970) as shown within the figure. C_i is the relative amount (ppm/ppb) of *n*-homologous series containing '*i*' carbons per molecule; the ratio incorporates five consecutive carbon numbers of the series (*i*, *i*+1, *i*+2, *i*+3, and *i*+4) and centres on the component with '*i*+2' carbon atoms. The value is greater or less than unity (dashed line) if odd or even carbon number predominates respectively. Note the disparity in the OEP trends for both classes of compounds. n.m = not measurable due to absence of one or more components.

4.7.2. *Hop-17(21)-enes*

Hopenes are the least abundant of all olefins detected in most oils. The concentration data and distribution ratios for the identified C_{30}-C_{35} hop-17(21)-enes are presented in Table 4.8. Figure 4.29 shows the m/z 367 trace in which the distribution patterns of the extended (C_{30}-C_{35}) hop-17(21)-ene series are illustrated in the containing representative oils. Their concentrations in these oils range from trace amounts to 14 ppm (Table 4.1). Identification was by mass spectral interpretation and comparison of relative retention times to their hopane counterpart on the m/z 191 mass chromatograms. For example, the two epimers of homohop-17(21)-enes (C_{31}-22*S*/*R*) elute right after moretane and before the C_{31} 17α(H),21β(H)-homohopanes (22*S* and 22*R* epimers). Correspondingly, other extended isomeric pairs elute before their extended hopane equivalents.

The abundance data (Table 4.8) and the C_{30}-C_{35} 22*S* and 22*R* isomer distribution illustrated by representative mass chromatograms (Figure 4.29) showed no resemblance in the abundances and distributions of homohopenes carbon number homologues; not even among samples from the same basin. Likewise, the extended hop-17,21-enes C-22 epimer ratios (22*S*/22*R*) varied widely across the sample set; that is, none of the two configurations predominated over the other. Figure 4.29 shows the distribution of the 22*S* and 22*R* epimers of the extended hop-17,21-enes for selected representative sample from each basin. The relative abundances of both epimers are highest in the Niger Delta oil; intermediate in the Beaufort-Mackenzie oil and lowest in the Kutei oil. Individual chromatograms shown are not representative of the distribution in other samples within a corresponding subset. The seeming variability in the distribution of the C_{30}-C_{35} homologues and its 22*S*/22*R* abundances suggest that these olefins could not have migrated with the oils from the source but may have been picked up by the migrating oil along its path.

Table 4.8 Concentration in parts per billion (ppb), and distribution data for C_{30}-C_{35} homologues of Δ17,21 hopenes for in all crude oils.

	C30	C31S	C31R	C32S	C32R	C33S	C33R	C34S	C34R	C35S	C35R	31-35S	31-35R					
Sample ID	Amount (ppb)													%C31	%C32	%C33	%C34	%C35
BMD01	1176	n.d	328	n.d	218	n.d	102	45	70	n.d	43	45	761	41	27	13	14	5
BMD02	673	n.d	383	n.d	145	n.d	69	n.d	30	n.d	16	n.m	643	60	23	11	5	2
BMD03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m	n.m
BMD04	98	52	64	21	33	n.d	36	n.d	n.d	n.d	n.d	73	133	56	26	17	n.m	n.m
BMD05	2100	36	641	n.d	165	n.d	76	n.d	43	n.d	8	36	933	70	17	8	4	1
CAN06	853	1502	1239	495	487	267	211	208	129	86	77	2558	2143	58	21	10	7	3
CAN07	312	105	82	20	7	n.d	n.d	n.d	n.d	n.d	n.d	125	89	87	13	n.m	n.m	n.m
CAN08	2521	3291	3883	863	986	409	494	317	334	265	255	5145	5952	65	17	8	6	5
KTM01	6	n.d	5	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	5	100	n.m	n.m	n.m	n.m
KTM02	48	14	33	n.d	15	n.d	n.d	n.d	n.d	n.d	n.d	14	48	76	24	n.m	n.m	n.m
KTM03	16	n.d	16	n.d	8	n.d	n.d	n.d	n.d	n.d	n.d	n.m	24	67	33	n.m	n.m	n.m
NDE01	796	329	709	76	267	n.d	142	n.d	70	n.d	28	405	1216	64	21	9	4	2
NDE02	n.d	292	187	163	115	74	43	48	21	21	n.d	598	366	50	29	12	7	2
NDE03	n.d	347	n.d	162	n.d	96	n.d	58	n.d	30	n.d	693	n.m	50	23	14	8	4
NDE04	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NDE05	n.d	101	39	54	n.d	34	n.d	14	n.d	n.d	n.d	203	39	58	22	14	6	n.m
NDE06	n.d	84	n.d	58	n.d	49	n.d	n.d	n.d	n.d	n.d	191	n.m	44	30	26	n.m	n.m
NDE07	n.d	147	74	91	53	42	n.d	39	n.d	n.d	n.d	319	127	50	32	9	9	n.m
NDE08	2153	363	1629	43	520	n.d	220	36	101	n.d	34	442	2504	68	19	7	5	1
NDW09	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NDW10	n.d	22	n.d	18	n.d	12	n.d	n.d	n.d	n.d	n.d	52	n.m	42	35	23	n.m	n.m
NDW11	264	412	490	120	232	37	94	20	59	n.d	32	589	907	60	24	9	5	2
NDW12	694	1955	1508	954	917	426	320	264	181	127	89	3726	3015	51	28	11	7	3
NDW13	231	992	891	480	503	268	175	218	133	128	110	2086	1812	48	25	11	9	6
NDW14	n.d	448	56	287	n.d	139	n.d	88	n.d	66	n.d	1028	56	46	26	13	8	6
NDW15	n.d	58	22	33	22	19	n.d	n.d	n.d	n.d	n.d	110	44	52	36	12	n.m	n.m
NDC16	n.d	420	307	182	144	95	64	55	32	19	14	771	561	55	24	12	7	2
NDC17	1253	2561	881	999	440	439	107	185	71	87	22	4271	1521	59	25	9	4	2
TRO01	2087	1605	1147	436	376	181	111	106	58	54	22	2382	1714	67	20	7	4	2
NSA02	249	808	534	762	742	588	488	423	348	455	347	3036	2459	24	27	20	14	15
NSA03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NSA04	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NSV05	10	42	38	38	37	39	30	25	19	12	6	156	130	28	26	24	15	6

The bottom of the table shows data for the reference oils, 3 of which also contain hopenes. Note the wide variation in the distribution across samples. 31-35S and 31-35–R = sum of each isomer in C_{31}-C_{35}; % C_{31}-C_{35} = (abundance of C_{31}, C_{32}, C_{33}, C_{34} and C_{35} hop-17(21)-enes (22*S*+22*R*)/total concentrations of all C_{31}-C_{35} (S+R))*100. n.d = not detected, hence some sample data were not measurable (n.m). The reference oils are the 'greyed' samples.

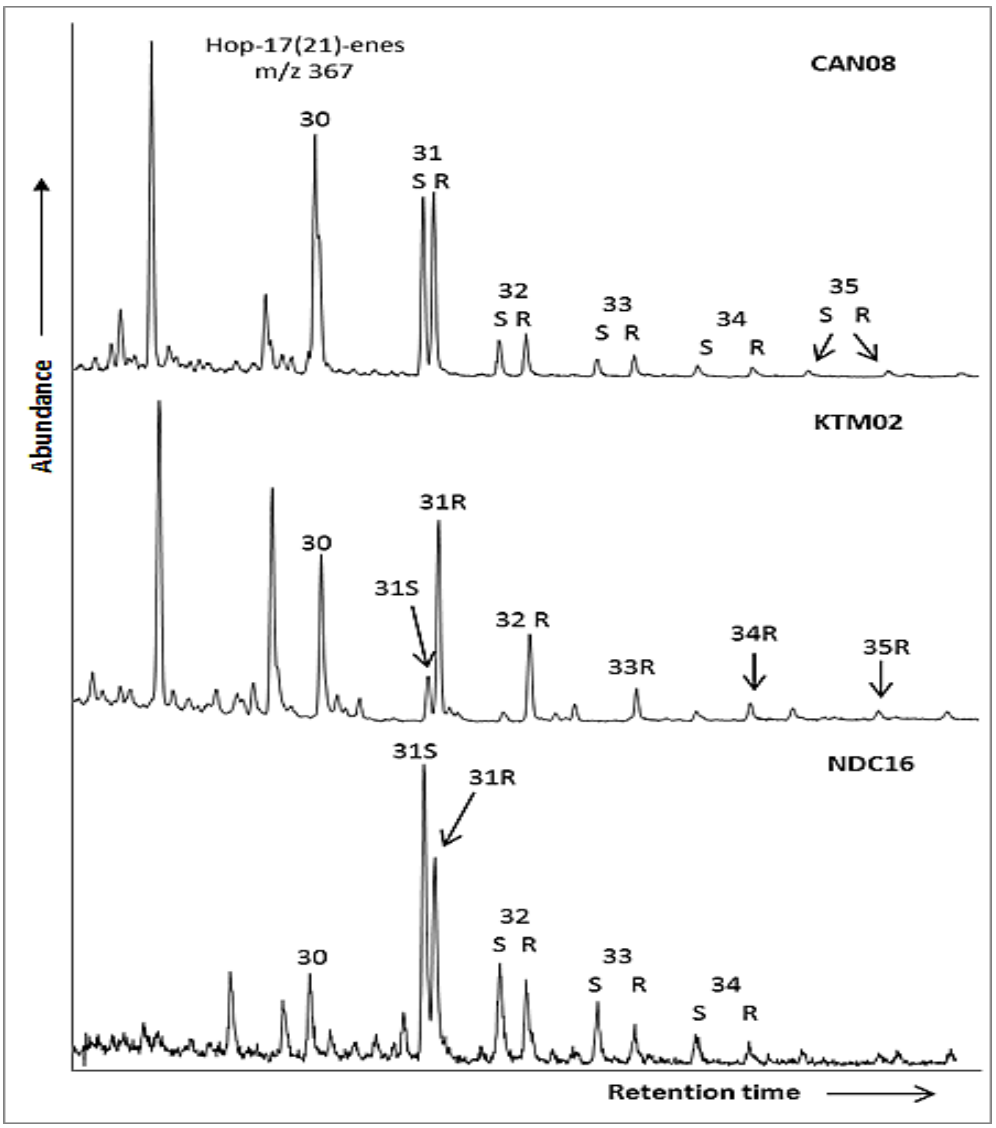


Figure 4.29 M/z 367 mass chromatograms showing the presence and distribution of hop-17(21)-enes. Their occurrence in Tertiary delta samples is represented in Beaufort-Mackenzie CAN08, Kutei KTM02 and Niger Delta NDC16 samples.

Plots of calculated values of percent C_{31}-C_{35} hopenes (Table 4.8) for all four sample subsets are shown in Figure 4.30. Comparing these profiles with those of their saturated counterparts (Figure 4.31) has revealed differences for each individual case study basin. The Beaufort-Mackenzie oils show variable hopene distributions as with the hopanes (Figure 4.30; Table 4.8). The Kutei samples are too few in number to ascertain any trends in the distribution patterns of the homohopenes, but the available data show that they have the lowest concentration of hop-17(21)-enes (11-110ppb; Table 4.7; Table 4.8) of the oils measured in this study and they were distributed over the C_{30}-C_{32} homologues only. The Niger Delta oils have closer-ranged and more uniform distribution especially for C_{31} and C_{32}; this continues to imply that these oils are more closely related by their sources. However, the differences shown in their hopene content and distribution may be the outcome of differences in their individual migrational paths. Most Niger Delta oils except a north east (NDE08), a northwest

(NDW12) and 2 samples from the central region of the delta have low abundances of C_{30}-C_{35} Δ17,21- hopenes as shown in Table 4.7 and Table 4.8.

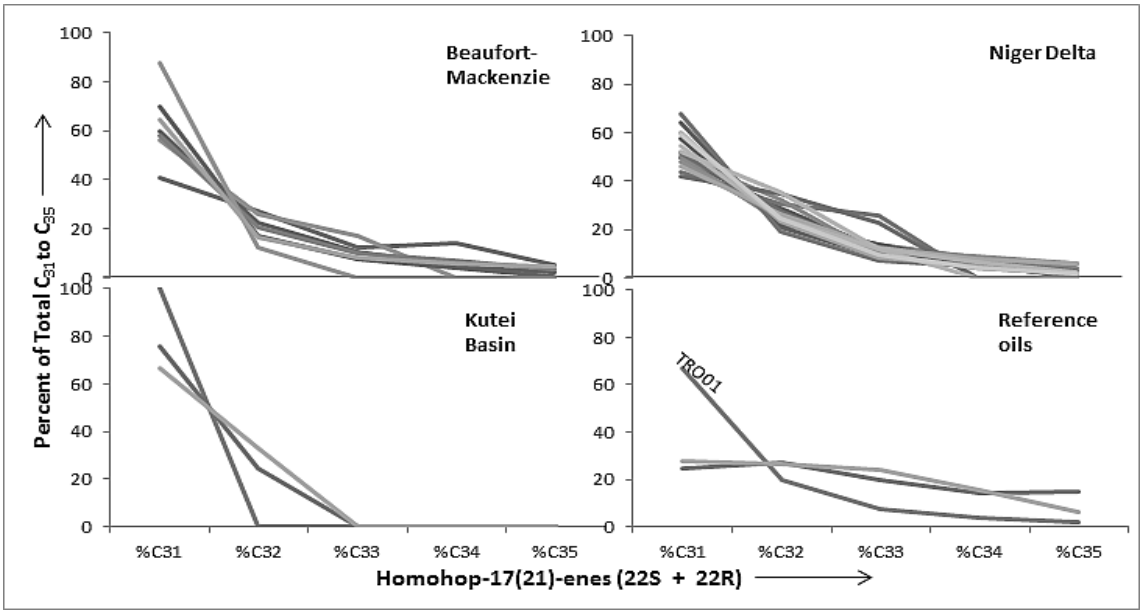


Figure 4.30 Distribution of extended C_{31} to C_{35} hop-17(21)-enes (22*R*+22*S*) in respective case study and reference oils.

In general, the distributions of C_{31-35} hop-17(21)-enes in the case study Tertiary oils contrast those in the hopene-containing reference oils (NSA02, NSV05) which reveal flatter distributions (14-28%) for C_{31} through to C_{34} series in both oils (Table 4.8). However, the mixed marine/terrigenous reference oil from Trinidad, (TRO01), though dominantly marine, exhibits the attributes of terrestrially-sourced oil which is, yet again, evidenced here by its hopene distribution comparable to those of the case study oils. Hopenes were not detected in two reference oils (NSA03 and NSA04).

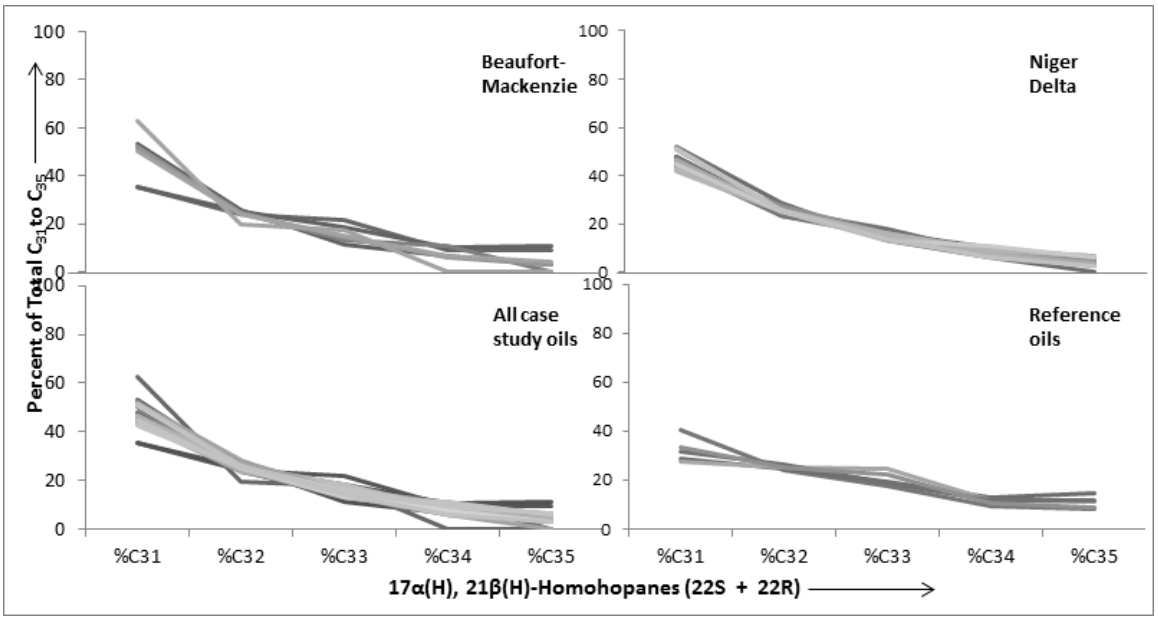


Figure 4.31 Homohopane (C_{31}-C_{35}) distributions in oil samples from Beaufort-Mackenzie and Niger Delta areas, and reference oil set. The 'All case study oils' plot excludes the reference oils.

4.7.3. *Oleanenes and Ursenes*

Of the 28 case study oils examined, 26 contained at least one of four oleanene isomers: olean-13(18)-ene, olean-12-ene, olean-18-ene and 18α-olean-12-ene (Table 4.9). Another pentacyclic triterpene, similar in structure to olean-12-ene and 18α-olean-12-ene (Figure 4.32), urs-12-ene, was identified in many of the samples but was most widespread in the Niger Delta oils (cf. Ukpabio *et al.*, 1994). The other two oils (BMD01 and BMD03) did not contain detectable amounts of any of these compounds. Their concentrations vary widely across Tertiary deltaic samples. Olean-18-ene is the most ubiquitous of the isomers occurring in all oleanene-containing samples. Representative m/z 218 mass chromatograms of unsaturated hydrocarbon fraction of the oils, on which urs-12-ene and the oleanene isomers are identified, are shown in Figure 4.33.

Table 4.9 Oleanene data and ratios for the studied oil samples.

	Ol-13(18)	Ol-12	Ol-18	Urs-12	18αOl-12	Olean	30-Olea	30-Hop	Ol-13(18)	Ol-12	Ol-18	Urs-12	18αOl-12	Ol'anes	Ol'enes
SampleID			(ppb)				(ppm)					(%)			
BMD01	n.d	n.d	n.d	n.d	n.d	n.m	162	191	n.m	n.m	n.m	n.m	n.m	46	n.m
BMD02	n.d	n.d	1462	n.d	n.d	1462	67	275	n.m	n.m	100	n.m	n.m	20	0.5
BMD03	n.d	n.d	n.d	n.d	n.d	n.m	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m	n.m
BMD04	n.d	n.d	350	n.d	n.d	350	21	179	n.m	n.m	100	n.m	n.m	11	0.2
BMD05	n.d	n.d	1647	n.d	n.d	1647	76	190	n.m	n.m	100	n.m	n.m	29	0.9
CAN06	5684	3154	6637	20612	6534	42621	265	857	13	7	16	48	15	24	4.7
CAN07	1197	635	603	4051	1314	7800	4	8	15	8	8	52	17	33	49.4
CAN08	9958	3973	5314	36823	8465	64533	290	972	15	6	8	57	13	23	6.2
KTM01	n.d	n.d	96	n.d	n.d	96	n.d	n.d	n.m	n.m	100	n.m	n.m	n.m	100
KTM02	n.d	n.d	958	n.d	n.d	958	31	37	n.m	n.m	100	n.m	n.m	46	2.5
KTM03	n.d	n.d	287	n.d	n.d	287	16	20	n.m	n.m	100	n.m	n.m	44	1.4
NDE01	n.d	n.d	4243	n.d	n.d	4243	1296	976	n.m	n.m	100	n.m	n.m	57	0.4
NDE02	n.d	n.d	5881	9375	1011	16267	914	576	n.m	n.m	36	58	6	61	2.7
NDE03	880	9657	5313	9724	1203	26777	1134	603	3	36	20	36	4	65	4.3
NDE04	n.d	n.d	3758	226	20	4004	494	415	n.m	n.m	94	6	n.m	54	1.0
NDE05	209	563	3628	6289	n.d	10690	625	360	2	5	34	59	n.m	63	2.9
NDE06	n.d	n.d	16368	26795	n.d	43163	723	622	n.m	n.m	38	62	n.m	54	6.5
NDE07	277	2008	8519	12360	1170	24334	788	517	1	8	35	51	5	60	4.5
NDE08	n.d	n.d	7083	n.d	n.d	7083	2520	1227	n.m	n.m	100	n.m	n.m	67	0.6
NDW09	n.d	n.d	812	344	44	1200	87	185	n.m	n.m	68	29	4	32	0.6
NDW10	62	71	238	339	37	747	154	347	8	10	32	45	5	31	0.2
NDW11	n.d	n.d	4112	n.d	n.d	4112	654	1454	n.m	n.m	100	n.m	n.m	31	0.3
NDW12	n.d	n.d	30838	1607	n.d	32445	728	592	n.m	n.m	95	5	n.m	55	5.2
NDW13	1568	8847	11382	23669	2232	47699	464	302	3	19	24	50	5	61	13.6
NDW14	1046	22274	4977	10289	1306	39892	291	418	3	56	12	26	3	41	8.7
NDW15	162	427	2963	4284	455	8292	393	556	2	5	36	52	5	41	1.5
NDC16	n.d	n.d	2943	5570	n.d	8513	659	646	n.m	n.m	35	65	n.m	50	1.3
NDC17	n.d	n.d	13000	1975	n.d	14975	619	633	n.m	n.m	87	13	n.m	49	2.3
TRO01	n.d	n.d	1142	2929	n.d	4071	32	188	n.m	n.m	28	72	n.m	15	2.1
NSA02	n.d	n.d	411	142	n.d	554	26	239	n.m	n.m	74	26	n.m	10	0.2
NSA03	n.d	n.d	n.d	n.d	n.d	n.d	4	64.0	n.m	n.m	n.m	n.m	n.m	6	n.m
NSA04	n.d	n.d	n.d	n.d	n.d	n.d	n.d	78.0	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NSV05	n.d	n.d	n.d	n.d	n.d	n.d	n.d	158	n.m	n.m	n.m	n.m	n.m	n.m	n.m

'Ol-13(18)', 'Ol-12', 'Ol-18' 'Urs-12' and '18αOl-12', respectively, are olean-13(18)-ene, olean-12-ene, olean-18-ene, Urs-12-ene and 18α-olean-12-ene, with amounts measured in ppb (ng/g oil), based on tentative identification; 'Olean' = Sum of all oleanenes+Urs-12-ene; 30-Olea and 30-Hop are C_{30}-(18α+18β)-oleanane and C30αβ-hopane quantities expressed in ppm (µg/g oil); %Ol13(18), %Ol12, %Ol18, %Urs12 and %18αOl12 are the oleanene isomers each normalised to C30αβ-hopane as a percentage; '%Ol'anes = (30-Olea/(30-Olea + 30-Hop))*100; %Ol'enes = (Olean/(Olean + 30-Hop))*100; 'n.d' and 'n.m' mean not detected and not measurable respectively and represented as zero values in related calculations.

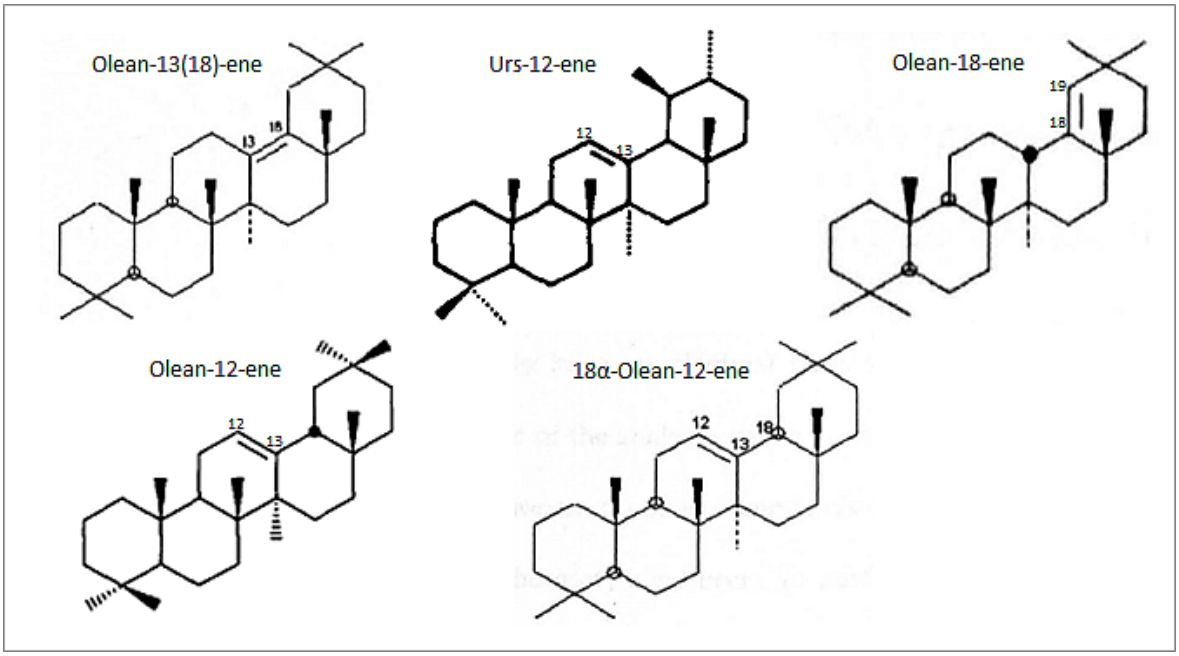


Figure 4.32 Structures of identified oleanene isomers and urs-12-ene as terrigenous molecular markers in oleanene containing samples (adapted from Rullkötter *et al.*, 1994).

The mass chromatograms (Figure 4.33) show that, while olean-13(18)-ene, olean-12-ene and olean-18-ene elute between the ααα20*R*-C_{28} and ααα-20*S*-C_{29} steranes (not prominent in the shown chromatograms) in these oils, urs-12-ene elutes just after the twin stereoisomers of αββ-C_{29} steranes (cf. Rullkötter *et al.*, 1994, Curiale, 1995) under the present column conditions. However, in some samples, 18α-olean-12-ene, where present, partially co-elutes with urs-12-ene; hence, it is important to note that the quantitation of both peaks is by manual integration as shown (Figure 4.33), and that measured amount of individual component is approximate. In general, the identification of urs-12-ene and the oleanene isomers on the m/z 218 trace is based on relative retention time and comparison with published works on these olefins (e.g. Peakman *et al.*, 1991a, Ukpabio *et al.*, 1994, Curiale, 1995). Again, these are tentative as the best possible means of identification was not employed.

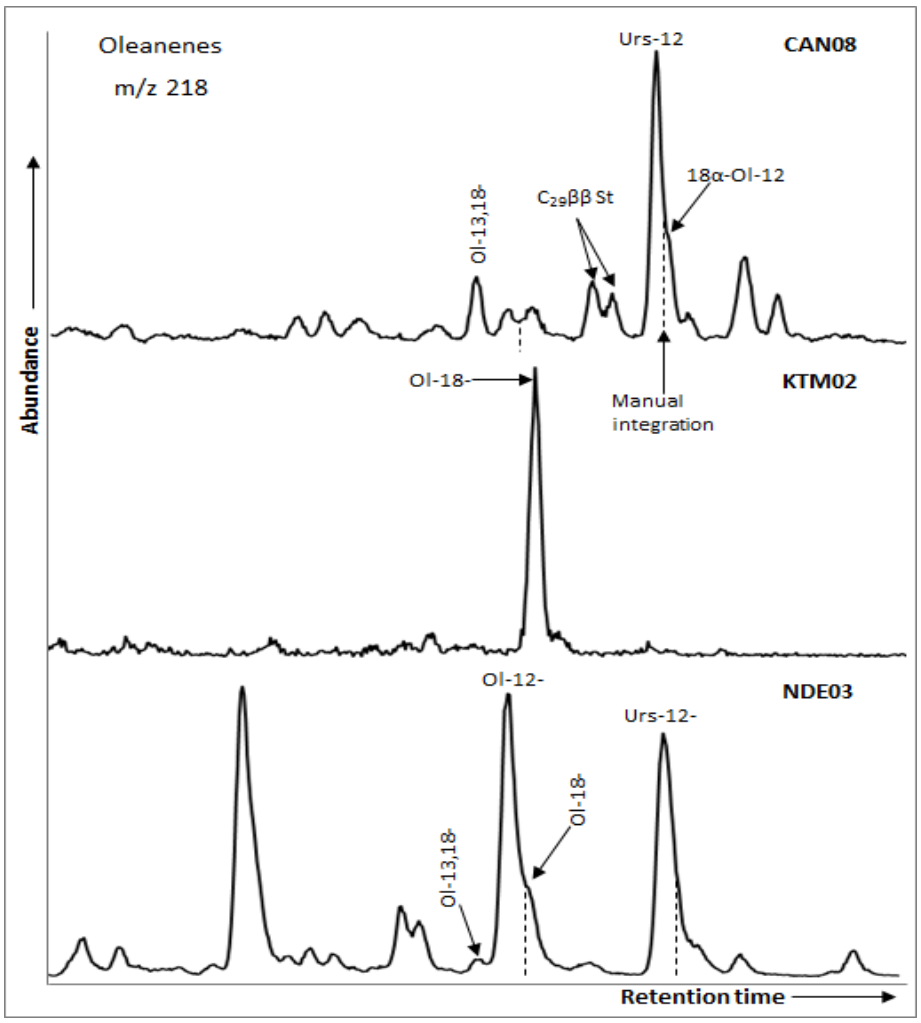


Figure 4.33 M/z 218 mass chromatograms showing distributions of oleanenes in 3 representative oleanene-containing oils. Peak identifications are by comparison of relative retention times with published work (Hoffman *et al.*, 1984, Rullkötter *et al.*, 1994, Curiale, 1995), and are labelled in order of their retention times as follows: olean-13(18)-ene, olean-12-ene, oleane-18-ene, urs-12-ene and 18a-olean-12-ene; hence, their identification in this study is tentative.

The extensive land plant signatures throughout the Tertiary oil dataset is evident from measured oleanene data (Table 4.9) which includes the contributions of terrigenous molecular markers normalized to C_{30}-hopane. Both saturated hydrocarbon and olefin data (Table 4.3; Table 4.9) have shown that oleanenes and ursenes are major components of many deltaic oils which usually occur alongside other indicators of land plant input in the oils such as oleanane and abundant C_{29} steranes (Peakman *et al.*, 1991a, Ukpabio *et al.*, 1994, Curiale, 1995). Their relative abundance in many of these mature oils, especially those which are believed to have been generated at high temperatures, such as the Niger Delta oils, meant that this group of olefins are more stable than other co-occurring olefins at these conditions (e.g. Niger Delta oils; Curiale, 1991, Rullkötter *et al.*, 1994, Eneogwe *et al.*, 2002).

Information on the origin of oleanene isomers found in these crude oils can be obtained when their relative abundances are plotted against each other (e.g. Figure 4.34). The occurrence of

these olefins is shown here to be prominent in Tertiary oils and/or samples with relatively high amounts of oleanane, but they are absent in many Cretaceous or older oils (Table 4.3 vs. Table 4.9). This is evident in their absence in three reference (NSA03, NSA04 and NSV05) North Sea (Jurassic Type-II sourced) oils in the sample set. Their abundance in TRO01 and NSA02 is expected because, though they are predominantly marine-sourced, these oils have consistently shown evidence of considerable amount of terrestrial organic matter input (e.g. Table 4.6; Figure 4.3). This observation agrees with the proposal by Curiale (1991) that oleanenes can function, not only as markers of organic matter input but also, are good distinguishing indicators of geologic age and history.

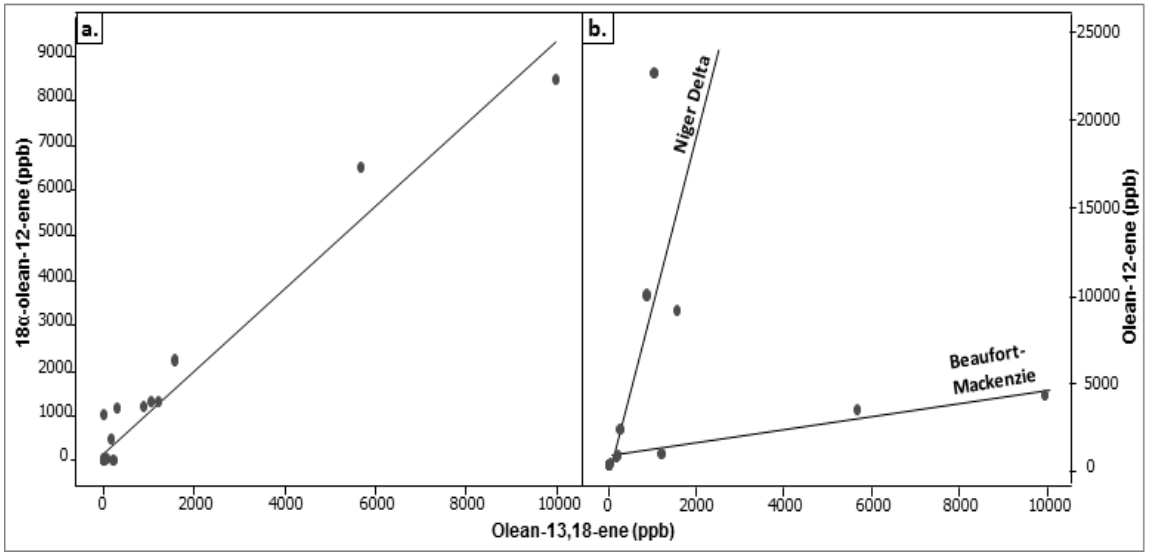


Figure 4.34 Cross-plots of the abundances of (a) 18α-olean-12-ene and (b) olean-12-ene versus olean-13(18)-ene, only for X-Y pairs of corresponding oleanene isomers in the containing samples only.

Occurrence and Origin

The thermal instability of olefins causes them to become hydrogenated at temperatures around those of onset of oil generation (Tissot and Welte, 1984); hence, they are not believed to originate directly from active source rocks (Hunt, 1979). Although, later studies have shown olefins to be present in oils generated at a temperature of more than 80^{o}C (Ukpabio *et al.*, 1994, Curiale, 1995), the low generation temperature hypothesis supports a major proposition of post-source origin (migration-contamination) for this class of hydrocarbons (e.g. Curiale, 1995). On the other hand, Eneogwe *et al.* (2002), in their study of several Niger Delta oils, argued against the migration-contamination hypothesis; they suggested that the oleanenes present in these oils are source-derived.

Olean-13(18)-ene, olean-12-ene and olean-18-ene are thought to be alteration products of higher plant triterpenoids (Hoffman *et al.*, 1984, Rullkötter *et al.*, 1994). Their occurrence

with other oleanoids demonstrates a significant contribution of terrestrial organic matter to the source facies of these oils (ten Haven *et al.*, 1992), hence, categorizing them as 'olefins of higher plant origin'. In their laboratory-simulated hydrogenation, acid-catalysed rearrangement, and correlation studies, ten Haven and Rullkötter (1988), Rullkötter *et al.* (1994) and Eneogwe *et al.* (2002) agreed that olean-12-ene is a direct precursor isomer from which olean-13(18)-ene and 18α-olean-12-ene are formed. In the following section correlation analyses, using the isomers of these compounds (both individually and summed, e.g. Figure 4.35; Figure 4.34; Figure 4.36; Figure 4.37) will help to reveal the presence or absence of any relationship that may be useful in elucidating the origin of these oleanoids in majority of the study oils.

Significance of occurrence in the study samples

Five oleanene-containing Beaufort-Mackenzie oils exhibit a consistent distribution of the oleanenes and urs-12-ene. Although their relative oleanene/oleanane content is generally lower than those of the Kutei Basin and Niger Delta oils (Table 4.9), the cross-plots (Figure 4.34b, Figure 4.35 and Figure 4.36a, d and e) reveal more similar distributions and correlations, than, for designated oleanene isomers vs oleanane (Figure 4.36). Many workers have suggested an early generation temperature for oils from Tertiary reservoirs of the Canadian Beaufort-Mackenzie (e.g. Curiale, 1991) by incidence of their olefin content, particularly the oleanenes. It was thus thought that any source-derived olefins in these oils would have withstood the relatively low temperature system.

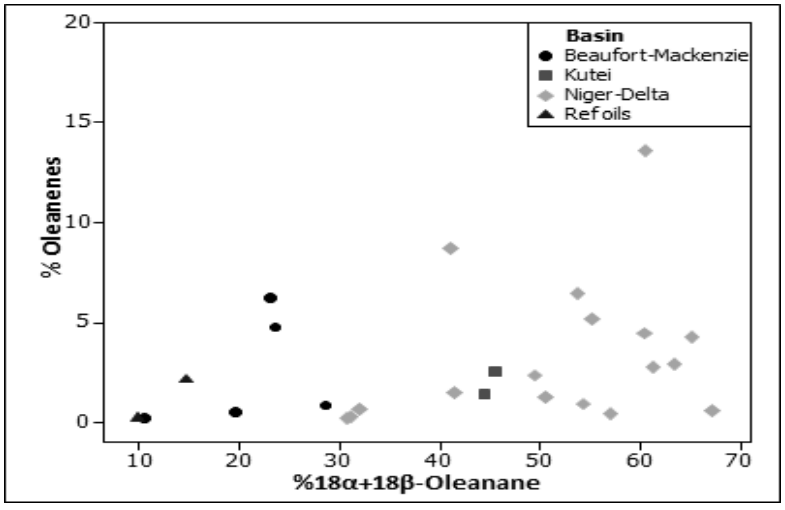


Figure 4.35 Relationship between %oleananes (18α-+18β) and %oleanenes (sum of all isomers normalised to C_{30}-hopanes as a percentage) in oleanene-containing samples; CAN07 (not on the plot) is an outlier (33, 49.4%).

For the moderately-mature to mature Niger Delta oils, correlations between the oleanene isomers are positive for the 18α-ol-12-ene and ol-12-ene versus ol-13(18)-ene plots (Figure

4.34). However, no positive relationship exists between the relative abundances of total oleanenes and C_{30}-oleanane (Figure 4.35), but, a comparison of the former relationship (Figure 4.34) with those in Figure 4.35 reveals a slight correlation in 'c' (ol-18-ene vs. oleanane) and probably 'd' (urs-12-ene vs. oleanane). Therefore, the non-correlation between the %oleanenes vs. %18(α+β)oleananes (Figure 4.35), especially in the Niger Delta oils, could have been influenced by the three oleanene isomers (olean-13,18-, olean-12- and 18α-olean-12-enes) that did not individually correlate with oleanane (Figure 4.36a, b and e). The abundance and, therefore, high thermal stability of oleanenes, and other olefins, in all analysed Niger Delta oils from source beds whose threshold temperatures could be up to 80ºC, as inferred by Ekweozor and Okoye (1980), is notable.

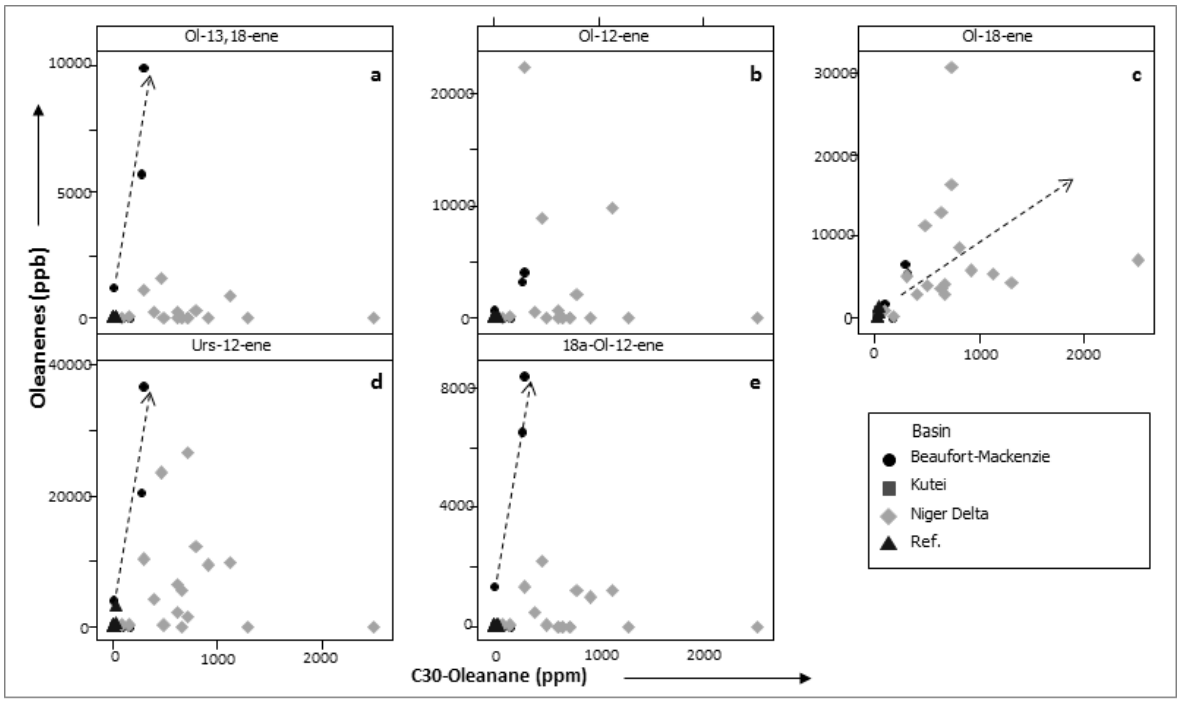


Figure 4.36 Cross plots of the abundances of individual oleanene isomers and urs-12-ene against C_{30}-Oleanane. Note the similarity in trends for ol-13(18)-ene, urs-12-ene and 18α-ol-12-ene vs C_{30}-oleanane in Beaufort-Mackenzie delta oils.

Cross-plots of the abundance of the isomers show that 18α-olean-12-ene and olean-12-ene are positively correlated to that of olean-13(18)-ene (Figure 4.34a, and b) but on a different scale for Beaufort-Mackenzie and Niger-Delta oils (Figure 4.34b). The implication of this is that olean-13(18)-ene and 18α-olean-12-ene are formed from olean-12-ene. This agrees with earlier findings from investigation of interactions between oleanene isomers in geological specimens (ten Haven and Rullkötter, 1988, Rullkötter *et al.*, 1994, Curiale, 1995, Eneogwe *et al.*, 2002). The slight correlation between olean-18-ene, as well as urs-12-ene, and the oleananes may be an indication that hydrogenation occurs mainly through olean-18-ene to form oleanane but at certain favourable conditions, or the combination thereof, as

temperature alone has not been able to account for such conversions as earlier believed (e.g. Tissot and Welte, 1984). It could also imply that inter-conversions between olean-18-ene and urs-12-ene are more feasible at the subsurface. An earlier suggestion that oleanane is most likely a product of diagenesis and some of these isomeric interactions (ten Haven and Rullkötter, 1988) is also supported by present observations. However, the relationship plots suggest that the oleanenes may be indigenous to the Beaufort-Mackenzie oils, but may also have been partially migration-derived, in a majority of Niger Delta oils.

In terms of relationship with maturity, a cross-plot of relative abundance of oleanenes (from m/z 218/191 mass chromatogram peaks) versus the 20*S*/(20*S*+20*R*) C_{27}- and C_{29} sterane maturity parameters (Figure 4.37) reveals no clear relationship between both ratios. This observation suggests that thermal maturity does not have any profound effect of decreasing the abundances of oleanene in the respective oils.

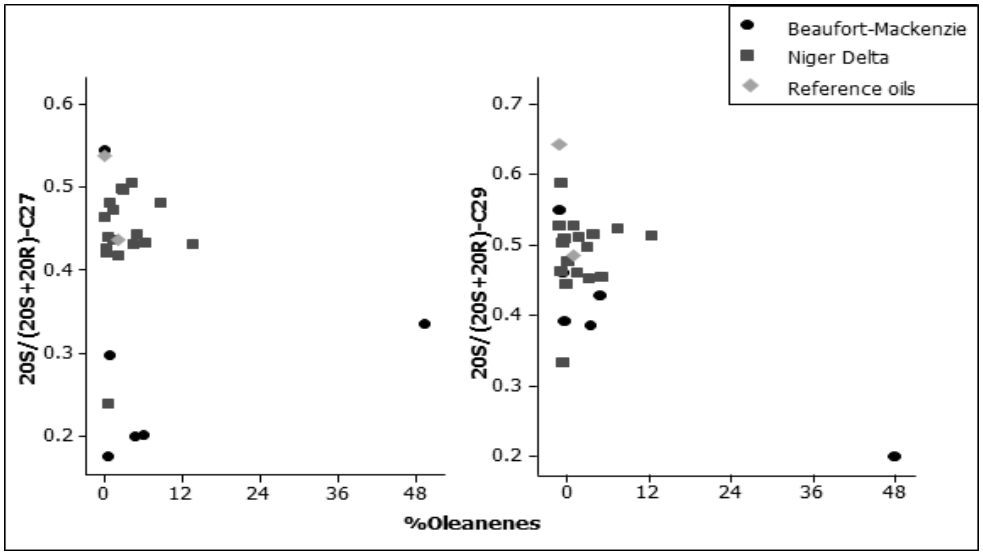


Figure 4.37 Cross-plot of 5α,14α,17α-20*S*/(20*S*+20*R*)-C_{27} and C_{29} sterane ratios vs %oleanenes for all oleanene-containing oils showing lack of correlation between maturity parameters and amount of oleanenes. The %oleanenes is the sum amounts of all isomers and urs-12-ene on the m/z 218 chromatogram, normalised to C_{30}-hopanes (after Eneogwe *et al.*, 2002 and , Curiale *et al.*, 2005).

4.7.4. *Diasterenes and Methyl-diasterenes*

Sterenes are absent, or are in concentrations below detection limits, in all the oils studied. However, diaster-13(17)-enes (20*R* and 20*S*) and 4β-methyldiaster-13(17)-enes (20*R* and 20*S*) are relatively abundant in most oils including all the reference oils (Table 4.10). Peak identifications were based on their relative retention times in the m/z 217/257/271 selected ion monitoring (SIM) mass chromatograms, as well as comparison of spectra with those in published data which were identified by co-injection with standard compounds (e.g. Peakman and Maxwell, 1988, Peakman *et al.*, 1989).

Table 4.10 Diasterene and methyl-diasterene data showing measured abundances for the oil samples containing, at least, two or more isomers of these classes of olefins.

	Diaster-13,17-enes (ppb)									4β-methyl-10α-diasterenes (ppb)							% 10α-20(S+R)-Diasterene		
Sample ID	C27β-S	C27α-S	C27β-R	C27α-R	C28α-S	C28α-R	C29α-S	C29β-R	C29α-R	C28-S	C28-R	C29-S	30S+29R	?C30x	C30-20R	?C30y	%C27	%C28	%C29
BMD01	69	432	241	1289	916	985	3448	3256	19021	109	187	181	604	633	211	666	7	7	86
BMD02	233	1036	183	1137	2071	2672	13699	2990	16824	158	130	361	654	320	237	497	6	13	82
BMD03	1	5	2	8	8	2	10	8	10	1	1	1	2	1	1	1	30	23	47
BMD04	170	727	105	637	1178	547	2547	499	1627	82	48	113	217	70	107	81	19	24	57
BMD05	245	1130	207	1197	2112	1798	9545	1760	8806	151	138	298	478	164	269	319	9	16	75
CAN06	1544	6193	722	4540	11407	12828	46763	8188	32281	754	754	2249	3310	498	1287	1115	9	21	69
CAN07	415	2028	453	740	3146	1646	8278	1252	4840	186	121	236	130	144	172	126	13	23	63
CAN08	2587	11371	982	10583	21414	19389	81093	16168	68163	1636	1903	3802	3907	1108	2882	3205	10	19	70
KTM01	7	22	4	20	37	31	159	22	118	2	2	8	13	6	3	4	11	18	72
KTM02	31	122	34	136	237	181	969	128	716	16	18	36	98	37	23	30	11	18	71
KTM03	42	112	23	107	166	165	767	113	567	13	10	22	33	11	10	15	12	18	71
NDE01	113	546	90	583	461	211	1234	227	793	51	50	85	156	32	91	87	29	18	53
NDE02	40	141	70	n.d	155	96	315	0	82				n.d				18	32	50
NDE03	34	97	105	n.d	196	91	468	60	188	n.d	34	31	61	44	n.d	n.d	9	28	63
NDE04					n.d								n.d					n.m	
NDE05	36	112	30	60	113	125	421	90	222	36	n.d	n.d	40	35	57	n.d	16	23	61
NDE06	33	125	79	n.d	115	117	605	94	126				n.d				11	21	67
NDE07	39	85	45	30	135	79	322	53	116				n.d				15	28	57
NDE08	69	341	59	394	363	177	1112	214	787	36	37	57	145	33	72	78	23	17	60
NDW09					n.d								n.d					n.m	
NDW10	n.d	15	14	n.d	21	14	44	n.d	29				n.d				12	29	59
NDW11	78	331	53	300	252	138	766	135	463	34	32	42	86	24	49	41	28	17	55
NDW12	271	1265	275	1006	1336	1115	4880	745	3079	129	169	341	476	99	320	230	18	19	63
NDW13	166	653	239	470	725	468	2160	520	1317	61	124	140	331	115	201	59	19	21	60
NDW14	18	27	254	n.d	n.d	58	113	43	449	35	34	31	230	60	n.d	n.d	4	9	87
NDW15	22	58	n.d	n.d	58	49	155	50	71				n.d				15	27	58
NDC16	79	322	54	40	346	157	751	36	279	38	n.d	67	109	n.d	n.d	n.d	19	27	54
NDC17	299	1189	468	388	1278	820	3160	414	1527	79	86	214	495	98	111	49	19	25	56
TRO01	260	1142	480	917	1269	483	2213	354	1611	87	128	193	570	158	118	105	27	23	50
NSA02	1617	6567	1070	5321	6088	2813	12416	2122	6632	1543	1556	2223	3518	1363	2467	1180	30	22	48
NSA03	170	730	81	590	607	254	1303	218	725	130	155	192	247	79	178	74	31	20	48
NSA04	21	105	11	29	90	26	153	26	114	25	18	20	13	9	35	8	26	22	52
NSV05	218	910	129	520	915	350	1642	167	753	191	138	242	124	103	204	82	28	25	47

Measurements were based on peak areas on m/z 257 (diasterenes) and 271 (methyl-diasterenes) mass chromatograms of olefinic fractions. 10α- and 10β- isomers were quantified in the case of diasterenes while the 4β-methyl-10α- stereochemistry is shown for 4-methyl-diasterenes. The integers (27,28,29,30) represents the number of carbon atoms in a component; α- and β- signify the stereochemistry at the C-10 positions for the diasterenes and 4-methyl-diasterenes; S and R represent the two epimers at position C-20; two peaks:?C_{30}x and ?C_{30}y are suspected to be C_{29}-methyl-diasterenes (C_{30}) but their structures could not be established. %C_{27}-C_{29} diasterenes are the relative abundance of C_{27}-C_{29}-10α (20*S*+20*R*)-diaster-13(17)-enes as percentage; n.d = not determined or not detected due to absence or below detection limit concentration of the respective compound(s), resulting in some non-measurable (n.m) data.

The distributions of $\Delta^{13,17}$-l0α(H)-diasterenes in the olefin fraction m/z 257 mass chromatograms are shown in Figure 4.38. The relative abundances of C_{27}–C_{29} diasterenes (10α-20*R*+20*S*) are plotted on a ternary diagram in Figure 4.39. The dominance by C_{29} components over C_{27} and C_{28} is illustrated here with relative abundance of C_{27}, C_{28} and C_{29} in the range 30-4%, 32-7% and 86-50%, respectively, in the case study oils containing diasterenes (Table 4.10). The measurement of the degree of C-20 isomerisation for the C_{27}-

C_{29} components was enabled by clear separation of the C_{28}- l0α(H)- $\Delta^{13,17}$-diasterene (20*R*) from the C_{29}-10α(H)-Δ13,17-diasterene (20*S*) on the HP-5 GC column phase (Figure 4.38). Histograms of the frequency of 20*S* and 20*R* epimers in Figure 4.40 reveal no significant differences between both epimers especially in the dominant C_{29} component. Ultimately, none of the isomers is shown to be distinctly isomerised over the other throughout the sample set.

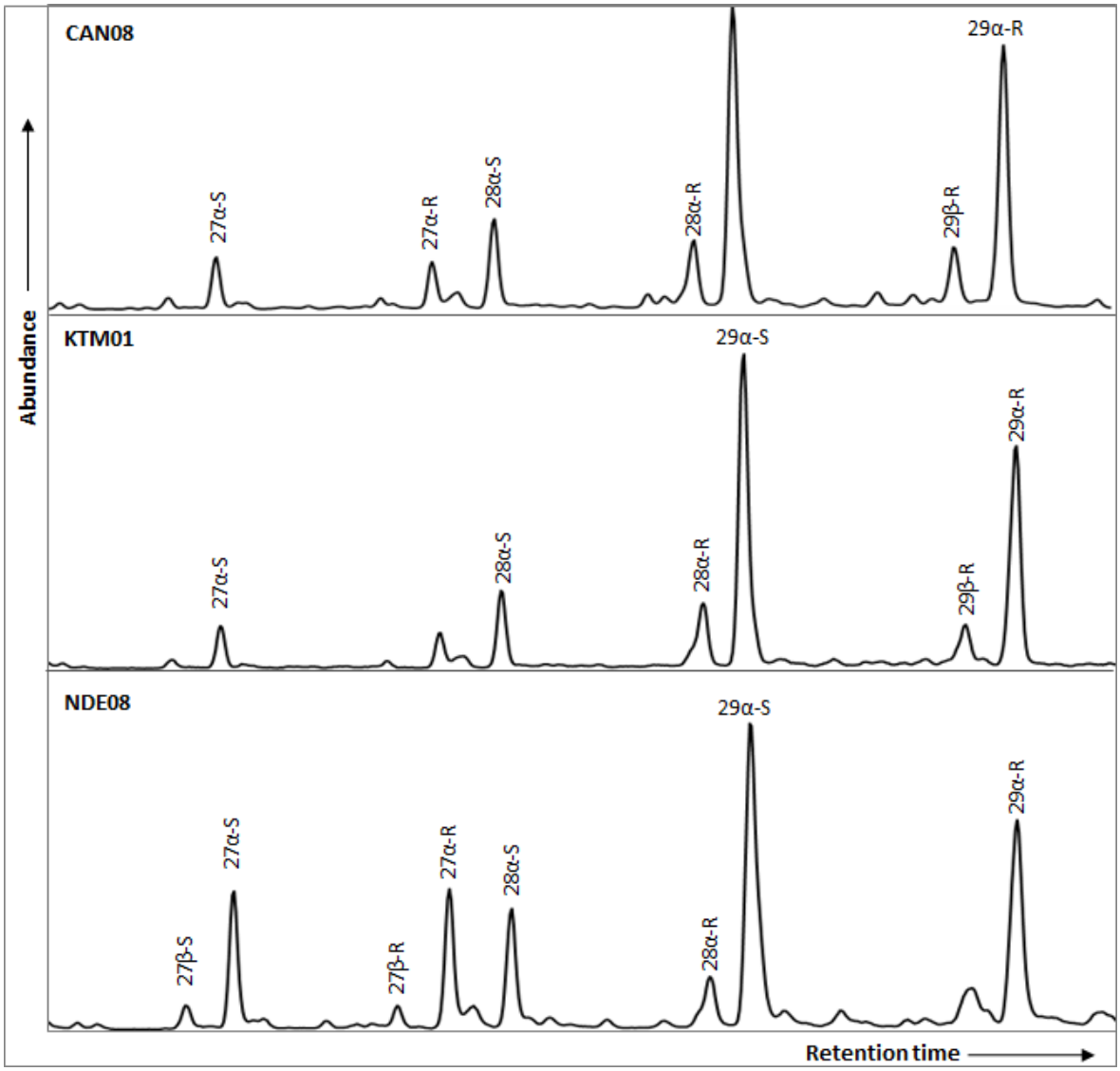


Figure 4.38 Partial m/z 257 mass chromatograms showing the distributions of the diaster-13(17)-enes in representative samples CAN08 (Beaufort-Mackenzie Delta), KTM01 (Kutei) and NDE08 (Niger Delta).

The oils of the Beaufort-Mackenzie Delta have the highest diasterene content except for BMD03, which has been shown, in earlier geochemical data (e.g. Table 4.2, Table 4.3), to be biomarker deficient, especially for higher molecular weight compounds. The Kutei Basin oils exhibit the lowest concentration of diasterenes but with the most consistent carbon number distribution. The dominance of C_{29} components (72%; Table 4.10) is still apparent in these oils. The abundances of individual C_{27}–C_{29} diasterenes vary considerably with wider

ranging distributions of the C_{27}-C_{29} components among the Niger Delta samples. Although the oils from this region reveal relatively high amounts of C_{29} components, very low to zero diasterenes were detected in a number of the oils (NDE04, NDE06, NDE07, NDE09, NDW10, and NDW15). 4-methyl-diasterenes were also not detected in the aforementioned samples (Table 4.10; Figure 4.40).

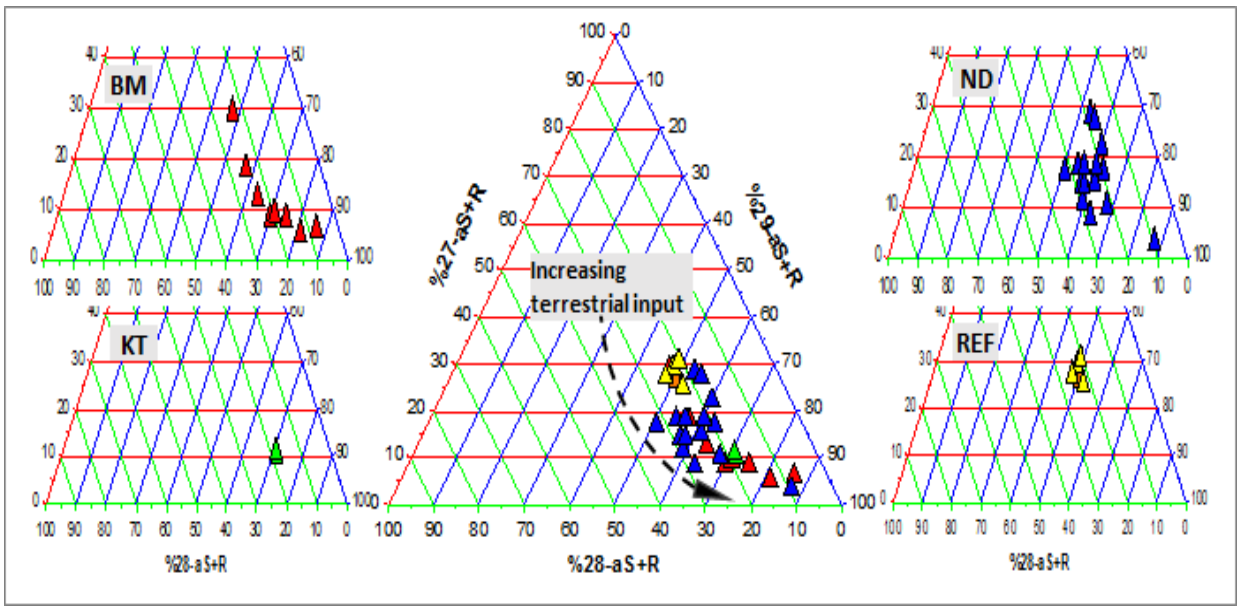


Figure 4.39 Ternary plots showing the relative abundance of C_{27}-C_{29}-10α-(20*S*+20*R*)-diaster-13(17)-enes in the olefinic fractions of the oil samples. The partial diagrams represent individual sample subset for Beaufort-Mackenzie (BM), Kutei (KT), Niger Delta (ND) and the marine oils (REF). Note the distinction between the marine and terrigenous (Tertiary) oils; as well as the high abundance and dominance of C_{29}- over C_{27}- and C_{28}-diaster-13(17)-enes) in most of the samples (adapted from Marynowski *et al.*, 2007).

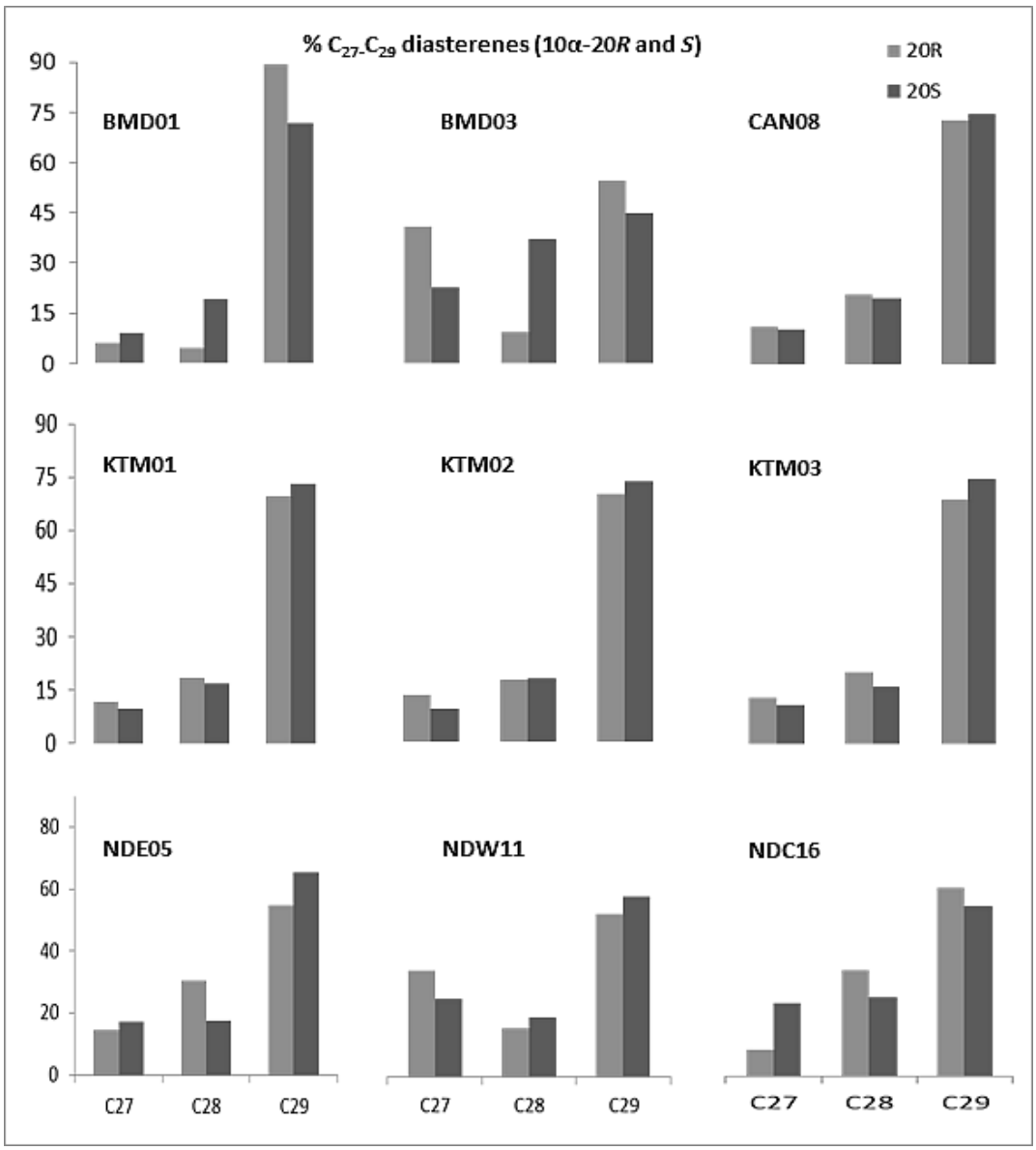


Figure 4.40 Histograms of carbon number distributions showing the degrees of C-20 isomerisation for $\Delta^{13(17)}$ l0α(H)-diasterenes in representative oils of the sample subsets (after Peakman *et al.*, 1989). Values were derived based on identified peak areas on the m/z 257 chromatogram.

The major series of 4-methyl-diasterenes having 4β-methyl-10α- stereochemistry is more abundant in all samples containing this class of olefins; this is most likely to be the result of the 4β-methyl-10α equatorial position being more stable (Peakman *et al.*, 1989), rather than the 4α-methyl position as earlier suggested by Rubenstein *et al.* (1975). There is also a minor series with the 4β-methyl-10β-stereochemistry at the axial position but they are not readily detected in the oils probably due to their decreasing stability and absence in the mature oils or their co-elution during GC-MS analysis (Peakman and Maxwell, 1988). Therefore, their resolution and complete separation from each other is dependent on the applied column phase and conditions. Representative distributions of 4-methyl-diasterenes are shown in Figure 4.41. Whilst the m/z 271 chromatograms show their overall distributions, peak identification of the C_{28}, C_{29} and C_{30} components was aided by superimposing and

comparing the m/z 271 mass chromatograms with those of m/z 369, m/z 383 and m/z 397 (M±15), respectively, in the samples.

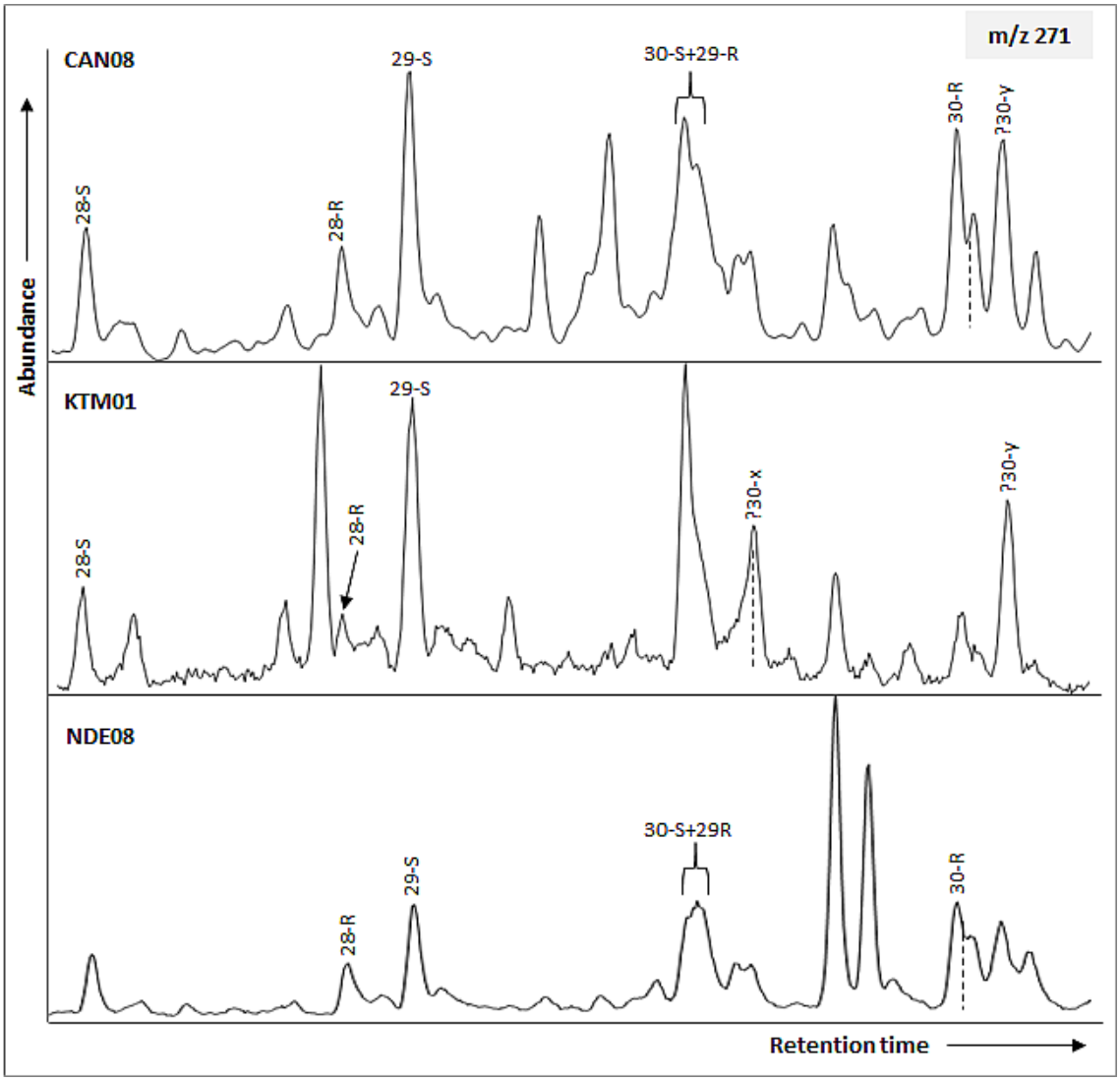


Figure 4.41 Partial m/z 271 mass chromatograms showing distributions of 4β-methyl-10α-diasterenes. The peaks denoted 30-x and 30-y are tentatively identified as isomers of methyl-C_{29}-diasterenes (C_{30}) whose configuration and structure could not established from their poorly resolved mass spectra.

Comparison between the abundances and distributions of diasterenes and 4-methyl-diasterenes in this study indicates a direct proportionality between the two groups. This relationship (Table 4.10; Figure 4.42) reveals that the occurrence or absence of 4-methyl-diasterenes is dependent on that of the diasterenes. In other words, the absence of diasterenes would mean the absence of 4-methyl-diasternes, but the reverse case does not hold; in addition, the samples (some Niger Delta oils; Table 4.10) that are shown to have very low diasterene content are most likely to lack 4-methyl-diasterenes. This finding suggests that the origin of 4-methyl-diasterenes is either similar to that of diasterenes or is a result of some form of rearrangement or conversion interactions between the diasterenes, methyl sterenes and their saturated counterparts with increasing diagenesis.

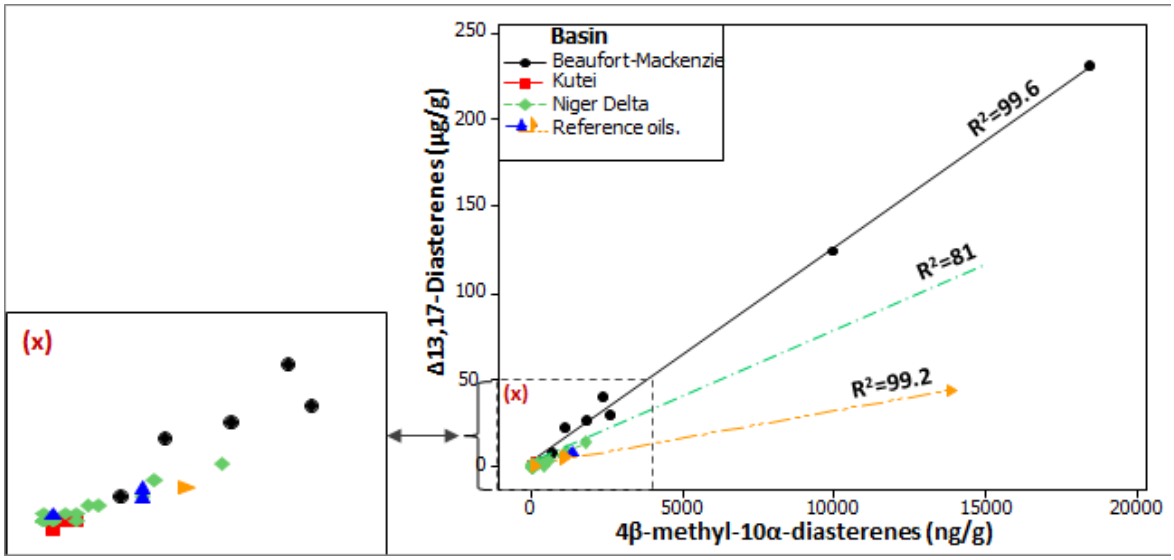


Figure 4.42 Cross-plots of total concentrations of identified diasterenes components versus corresponding 4-methyl-diasterenes showing the relationship between both groups of compounds. The inset plot (x) on the left shows an enlarged diagram of marked spot in the main plot, for a clearer view of correlation trends in the sample sets. Note the level of correlation within the 3 case study sample subsets as seen in the R-square values.

Significance and Implication on Source Assessment

The diasterene compounds, regardless of their source, depositional environment and thermal maturity, have been identified as one of the major and most widespread olefin compound groups in most study samples. Their dominance over sterenes, in the mature oils, may be due to a proposed early diagenetic acid catalysed backbone rearrangement processes of sterenes (Rubenstein *et al.*, 1975). High concentrations of C_{29}-diaster-13(17)-enes have been associated with an increase in terrestrial input and hence, they are used to provide supporting data concerning the source of OM (cf. Brassell *et al.*, 1986). However, some Niger Delta samples have been shown here (Table 4.10) to have very low or undetectable diasterene contents. There are exceptions to the generally accepted view that C_{29} components are derived solely from higher plants (Peters and Moldowan, 1993). For example, if the increase in concentration of the C_{29}-diaster-13(17)-enes indicates an increase of terrestrial input, then the reasons why they are lacking in some of the dominantly Tertiary deltaic oils and relatively abundant in all the marine reference oils is unclear. Possible reasons are: that these diasterenes may not have been wholly source-derived; that there are other factors responsible for the incorporation of diasterenes to the source organic matter; or that one of such geological factors involves migration and its effects on molecular composition of certain oils. Results from the whole olefin data (Table 4.7) have shown that most of the oils do not contain any class of olefins in isolation and that the presence of olefins indicative of low

thermal maturity alongside source-derived olefins is a better indication that mature oils containing these unsaturated compounds exhibit attributes of migration-contamination.

All the reference, marine oils contain both diasterenes and 4-methyldiasterenes. However, the difference between their diasterene contents and those of the case study oils are: the relative abundance of the C_{27} components which are somewhat higher than those of the case study samples and; the consistent close-ranging C_{27} (26-31%) to C_{29} (47-52%) distribution in these oils (shaded samples in Table 4.10). Their occurrence in reference oils is also evidence that diasterenes are not typical of only Tertiary systems but they are mostly indicative of source of organic matter input.

Ultimately, the occurrence of oleanenes, as well as hop-17(21)-enes and high amounts of diasterenes reveals a high likelihood of migration-induced compositional changes, with, perhaps, some contributions from other significant geologic factors (e.g. biodegradation), in many of these samples (cf. Curiale, 2002). For the Kutei Basin samples, the present findings are not conclusive due to limited samples. However, reference to previous studies on the Kutei oils including indications of a complex petroleum system and geochemistry (e.g. Satyana *et al.*, 1999, Curiale *et al.*, 2005), suggests both source and migration influences in the geochemical characteristics of these Miocene reservoired oils, which is supported by available olefin data.

4.8. Carboxylic Acids

Acid fractions were extracted from the oils by procedures described in detail in the previous chapter. Procedural blanks were analysed alongside the case study samples. One blank sample was run for every batch of up to seven samples. No significant contamination was observed in blank runs as evidenced by the very low or no peak responses in the gas chromatograms of 3 blank acids fractions from 3 different batches (Figure 4.43). Hence, the amount contributed by contaminants (between 1 and 15ppm), where present, were mostly insignificant, and this was subtracted from the calculated values.

The acidic components that were observed in the oils were the linear (*n*-acids) and hopanoic acids (HAs). These acids were identified as fatty acid methyl esters with the aid of published GC and GC/MS data including relative retention times of individual components and isomeric distributions of hopanoic acids (e.g. Schmitter *et al.*, 1978, Jaffé *et al.*, 1988a, 1988b).

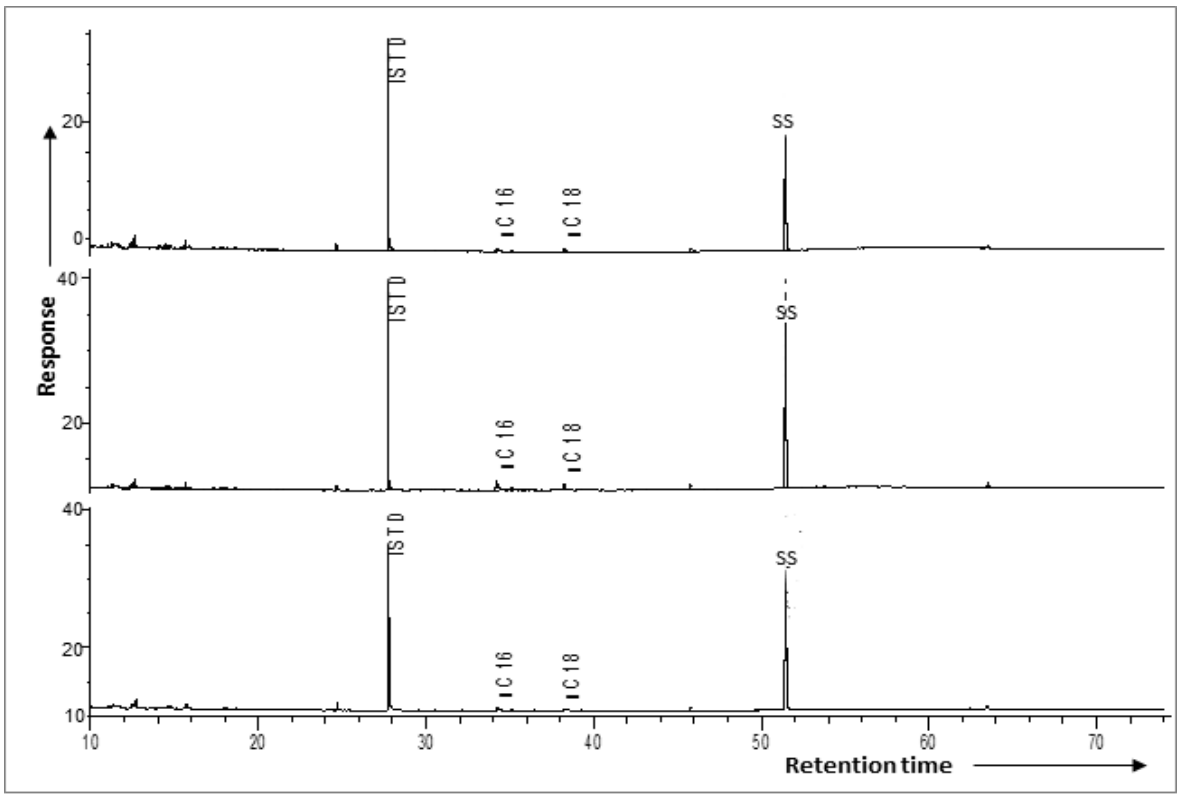


Figure 4.43 Gas chromatograms of 3 different blank acid fraction analyses showing the authenticity of acidic content of studied oils. One procedural blank was run with every batch of up to 7 samples. Peak responses of key components are relatively very low or absent. Detected *n*-C_{16} and *n*-C_{18} are negligible, and no lower or higher homologues than these were detected. The peaks, ISTD and SS, represent the internal standard and surrogate standard respectively.

Examples of the distributions of carboxylic acids in the studied oils are shown in Figure 4.44. It is worthy to note that some of the analysed Beaufort-Mackenzie (BMD01 and BMD02) and Niger Delta (NDW11) samples exhibited severe biodegradation (see Table 4.1, Figure 4.17) indicated by the removal of *n*-alkanes as clearly evidenced by large UCM humps in the respective chromatograms (Appendix III-c). It is therefore, likely that the high carboxylic acid content in these oils, (e.g. NDW11) is influenced by biodegradation. However, unusually high quantities of linear acids were also measured in many non-degraded oils of, especially, the Niger Delta (e.g. NCW09, NDE04, NDC17, see e.g. Figure 4.17). This could very likely mean that the origin of these components are either migration-derived, source-related, or both. Quantitative data on the carboxylic acids, and some derived *n*-acid and isoprenoid acids are shown in Table 4.11. Due to insufficient sample volumes, acid analysis was not carried out for two Niger-Delta oils (NDE07, NDC16) and three oils (CAN06, CAN07, CAN08) of the Beaufort-Mackenzie Delta; hence they are not represented in the acid data table. For the rest of the samples, total carboxylic acid concentration (including the isoprenoid acids), the total *n*-acids and hopanoic acid concentrations were obtained and are shown (Table 4.11).

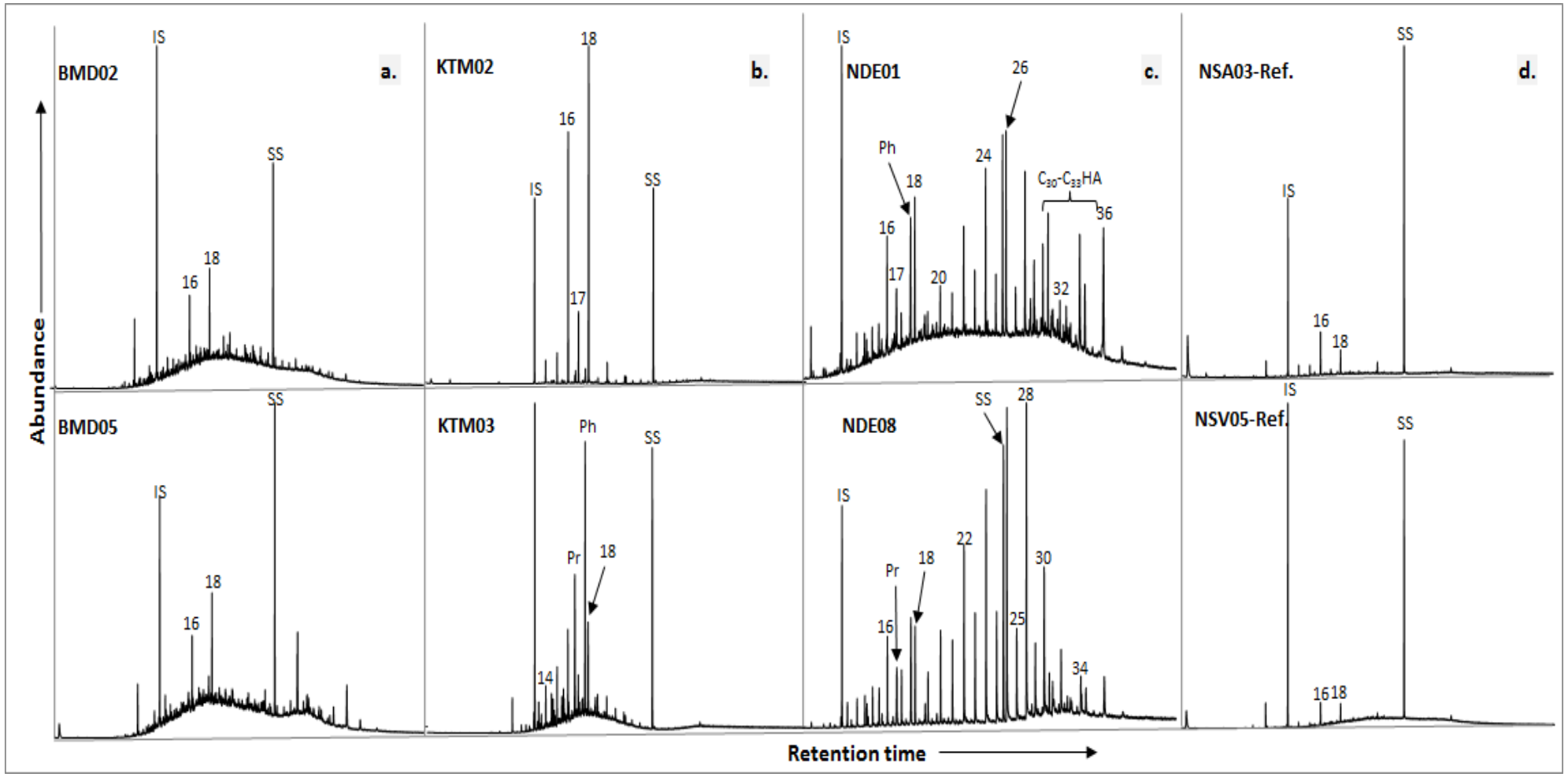


Figure 4.44 Total ion chromatograms (TIC) showing the distributions of carboxylic acids (as acid methyl esters) in selected pairs of representative samples (a, b, and c) from all three case study deltas. The fourth pair (d: NSV05 and NSA03) are typical reference (marine) oils. IS and SS are the internal (methyl ester of 1-phenylcyclohexane carboxylic acid) and surrogate (5β-cholanic acid methyl ester**)** standards respectively; the integers represent the carbon chain length of the linear/normal acid methyl esters; Pr and Ph are the pristanic and phytanic (isoprenoid) acids, and elute just before *n*-C_{17} and *n*-C_{18} acid-MEs respectively. The MEs of cyclic hopanoic acids are shown to elute towards the end of separation. The x-axes for each pair of TICs are scaled equally.

Table 4.11 Quantitative data on *n*-acids and hopanoic acids (as methyl esters), and saturated acid-based ratios and parameters for the acid-containing oils.

Sample ID	SCA (µg/g)	LCA (µg/g)	Pr-acid (µg/g)	Ph-acid (µg/g)	TnA (µg/g)	HA (µg/g)	TαβHA (ng/g)	TβαHA (ng/g)	TββHA (ng/g)	TA (µg/g)	CPI-1	CPI-2	CPI-3	C28/C18	Pr/Ph	Pr/nC17	Ph/nC18	C17/C27
BMD01	176	251	21.5	11.2	392	16	2075	3647	10249	441	0.93	1.17	0.96	0.26	1.92	1.07	0.16	0.95
BMD02	107	106	12.7	7.6	167	7	821	904	4792	194	0.99	0.83	1.15	0.11	1.67	0.85	0.22	3.11
BMD03	132	30	2.4	3.5	n.d	n.d	n.d	n.d	n.d	6	1.12	1.10	1.24	0.05	0.69	0.30	0.13	4.92
BMD04	37	17	n.d	0.4	n.d	8	1174	n.d	7151	9	2.84	2.23	2.41	0.13	n.d	0.00	0.02	1.09
BMD05	58	43	9.2	2.0	75	22	1609	1984	18451	108	0.92	0.85	0.89	0.15	4.56	2.06	0.10	1.36
KTM01	47	1	2.5	2.6	16	n.d	n.d	n.d	n.d	21	n.m	n.m	n.m	n.d	0.97	2.56	0.13	n.m
KTM02	208	25	4.0	6.1	51	1	269	309	347	62	1.53	1.68	1.44	0.02	0.65	0.19	0.06	18.32
KTM03	82	61	60.9	105.4	89	n.d	n.d	n.d	n.d	255	1.99	0.85	0.90	0.02	0.58	9.74	3.79	28.21
NDE01	165	556	47.5	66.5	397	120	20845	16635	82633	631	2.65	2.22	2.62	1.31	0.71	1.95	1.22	0.96
NDE02	77	286	17.8	35.4	272	77	13077	8513	55176	402	2.41	1.94	2.17	1.71	0.50	1.82	1.53	0.60
NDE03	70	315	14.0	18.9	374	30	3758	4172	22498	437	2.31	1.58	2.04	2.82	0.74	1.67	1.20	0.45
NDE04	178	375	19.8	24.1	546	57	8762	5527	42310	647	3.07	2.28	2.75	0.64	0.82	1.43	0.29	0.77
NDE05	27	97	7.3	11.4	110	6	1779	1925	2613	135	2.07	1.35	1.51	1.66	0.64	5.31	1.55	0.25
NDE06	108	395	38.7	49.4	495	37	8349	7182	21118	620	1.75	1.39	1.83	1.76	0.78	1.77	2.33	0.94
NDE08	93	612	21.6	38.8	527	38	7890	6430	23486	625	3.06	1.91	2.54	4.12	0.56	1.55	1.65	0.40
NDW09	6477	68	6.0	10.7	6510	6	744	n.d	5687	6533	2.84	1.74	2.08	0.15	0.56	0.95	0.16	1.69
NDW10	262	130	18.9	21.2	380	13	4039	3491	5361	433	1.97	1.45	1.81	0.27	0.89	2.16	0.44	1.19
NDW11	1213	69	14.7	46.9	1204	74	13971	19685	40054	1339	0.83	1.14	1.12	0.13	0.31	1.14	1.14	1.91
NDW12	50	345	19.3	25.2	383	17	5289	5071	6723	445	2.60	1.54	1.90	5.31	0.76	3.35	2.47	0.29
NDW13	145	141	36.4	19.3	258	59	7982	8896	42175	373	2.59	2.35	2.63	0.30	1.89	2.87	0.47	2.66
NDW14	48	102	5.0	6.9	144	38	7216	5613	24938	194	1.86	1.24	1.42	0.63	0.73	1.39	0.43	0.78
NDW15	87	313	22.5	32.6	29	11	4741	5014	1499	95	2.25	1.38	1.61	2.42	0.69	2.34	1.65	0.48
NDC17	177	425	25.4	38.3	531	12	4335	4407	3424	607	2.82	1.65	2.14	0.94	0.66	1.62	0.59	0.70
TRO01	79	82	14.6	14.5	126	22	7848	5583	9025	178	1.70	1.36	1.68	0.44	1.01	2.51	0.89	1.22
NSA02	141	27	6.9	1.4	139	10	n.d	n.d	9691	157	1.95	1.33	1.49	0.04	4.82	1.72	0.02	4.96
NSA03	20	4	0.6	0.9	16	n.d	n.d	n.d	n.d	17	1.21	1.67	1.67	0.04	0.74	0.40	0.19	8.62
NSA04	40	4	0.8	0.8	n.d	n.d	n.d	n.d	n.d	2	2.54	1.43	1.60	0.01	1.08	0.47	0.05	11.54
NSV05	11	4	0.6	0.6	n.d	n.d	n.d	n.d	n.d	1	1.74	1.00	1.50	0.11	1.12	0.74	0.17	3.54

SCA and LCA = estimated short chain (sum C_{11}-C_{19}) and long chain (sum $\geq C_{20}$) linear acids respectively; TnA = 'corrected' (C_{11}-C_{34}) total *n*-acids; HA = sum (C_{30}-C_{33}) hopanoic acids; TαβHA, TβαHA & TββHA = total of 22*S*+20*R*-$C_{30\text{-}33}$- αβ, βα and ββ HA isomers respectively; TA = TnA +Pr+Ph+HA; CPI-1, CPI-2 and CPI-3 = carbon preference indices: $(2\times C_{24})/(C_{23}+C_{25})$, $(2\times C_{28})/(C_{27}+C_{29})$, and $(C_{24}+C_{26}+C_{28})/(C_{25}+C_{27}+C_{29})$ respectively; C_{28}/C_{18} and C_{17}/C_{27} = ratios of corresponding *n*-acids; Pr/Ph, Pr/nC_{17}, Ph/nC_{18} = acid ratios derived from pristanic and phytanic (isoprenoid), and C_{17}, C_{18} *n*-acids; n.d/n.m= not detected/not measurable due to absence of one or more component in the expression; shaded column = reference oils. Acid data were not measured for CAN06, CAN07, CAN08, NDE07, and NDW16 due to insufficient sample quantity needed for the acid analysis.

4.8.1. *The linear and acyclic isoprenoid acids*

The m/z 74 mass chromatograms in Figure 4.45 show the distribution of the acyclic acids in representative oils of all three sample subsets. The distributions are dominated by wide ranging homologous series of saturated *n*-acids (C_{12}-C_{34}) with summed concentrations ranging from trace amounts to about 1200 µg/g (Table 4.11). An outlying total concentration of ~6500 µg/g (TnA, Table 4.11) with over 99% C_{12}-C_{19} short chain acids (SCA) was recorded for a Niger Delta oil (NDW09); a repeat isolation and analysis reproduced similar results. The distribution of saturated fatty acids across the sample suite is either unimodal or bimodal. For unimodal distributions, three maxima were observed at C_{12}, C_{16} and C_{18}; samples with bimodal distribution have maxima at C_{16} or C_{18} and a wider range of long chain acids maximising between C_{24} and C_{30} carbons, suggestive of a mixed origin. The first (short-chain) maximum is, however, clearly dominant (Figure 4.45) in many of the samples. It is interesting to note that the most abundant peaks in the chromatograms are commonly those of the C_{16} and C_{18} saturated acids.

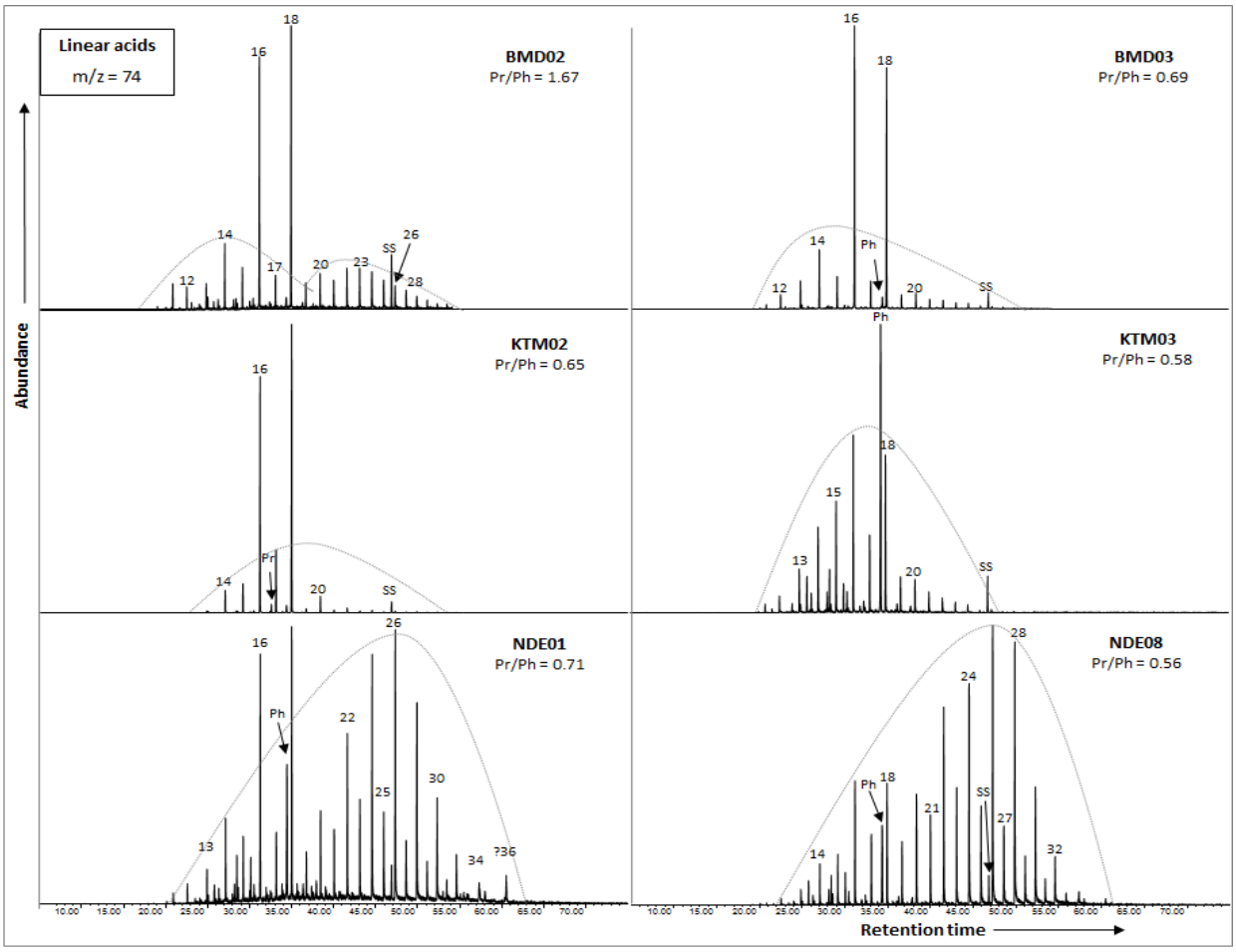


Figure 4.45 m/z 74 mass chromatograms showing the distributions of straight chain and isoprenoid fatty acids (as methyl esters) in the case study oils. 'SS' is the recovery standard peak. The sketched curves on the chromatograms shows the type of distribution in like samples from the 3 representative basins. Note how mixed (usually bimodal) distributions differ from more terrigenous oils by the skewness of the curves.

Figure 4.46 shows the distribution of the *n*-acids for representative samples. Short chain, long chain and isoprenoid acid data were estimated for the purpose of comparisons and do not exclude amounts of possible linear C_{16} and C_{18} contaminants, but these are generally insignificant as previously shown (Figure 4.43). The patterns in the short chain (SCA) and/or long chain acids (LCA) could be an indication of the depositional environment of the oils (e.g. Jaffé and Gallardo, 1993). The Beaufort-Mackenzie oils display intermediate distributions between both end members (marine and terrigenous). While acid distributions in the five analysed BMD oils are indicative of samples from mixed sources, BMD03 and BMD04 show characteristics of predominantly marine oils (Figure 4.45, Table 4.11). This is also shown by the C_{28}/C_{18} ratios which generally distinguish between the terrigenous (0.50-5.3); mixed (0.11-0.44) and the marine (<0.01-0.10) oils. This classification is based on pattern of data derived here, and is not applied to the Kutei oils which have been shown to be low in high molecular weight compounds ($>C_{26}$). Acid distributions in the oils of the Niger delta Basin show a wide range of abundances of SCA and LCA, with the C_{28}/C_{18} *n*-acid ratio also varying from 0.13-5.31 (Table 4.11). However, higher values of this ratio with long-chain acids dominating the distribution may also signify the result of a geochromatography effect which causes the retention of the SCA by the rock matrix during migration due to polarity differences between the acids (Jaffé *et al.*, 1988b, Jaffé and Gallardo, 1993). The OEP carbon number distributions (Figure 4.47) for these (Niger Delta) oils are very consistent throughout the sample set as opposed to the wider variations in the Beaufort-Mackenzie and Kutei Basin samples. It should be noted that the oil condensates of the Kutei Basin have very low concentrations of high molecular weight biomarkers and related acid parameters and ratios could not be measured for these samples (Table 4.11). Hence, linear short-chain acids are seen to dominate the distribution in these oils except KTM03 which reflects a distribution of both *n*-acid end members (Figure 4.46).

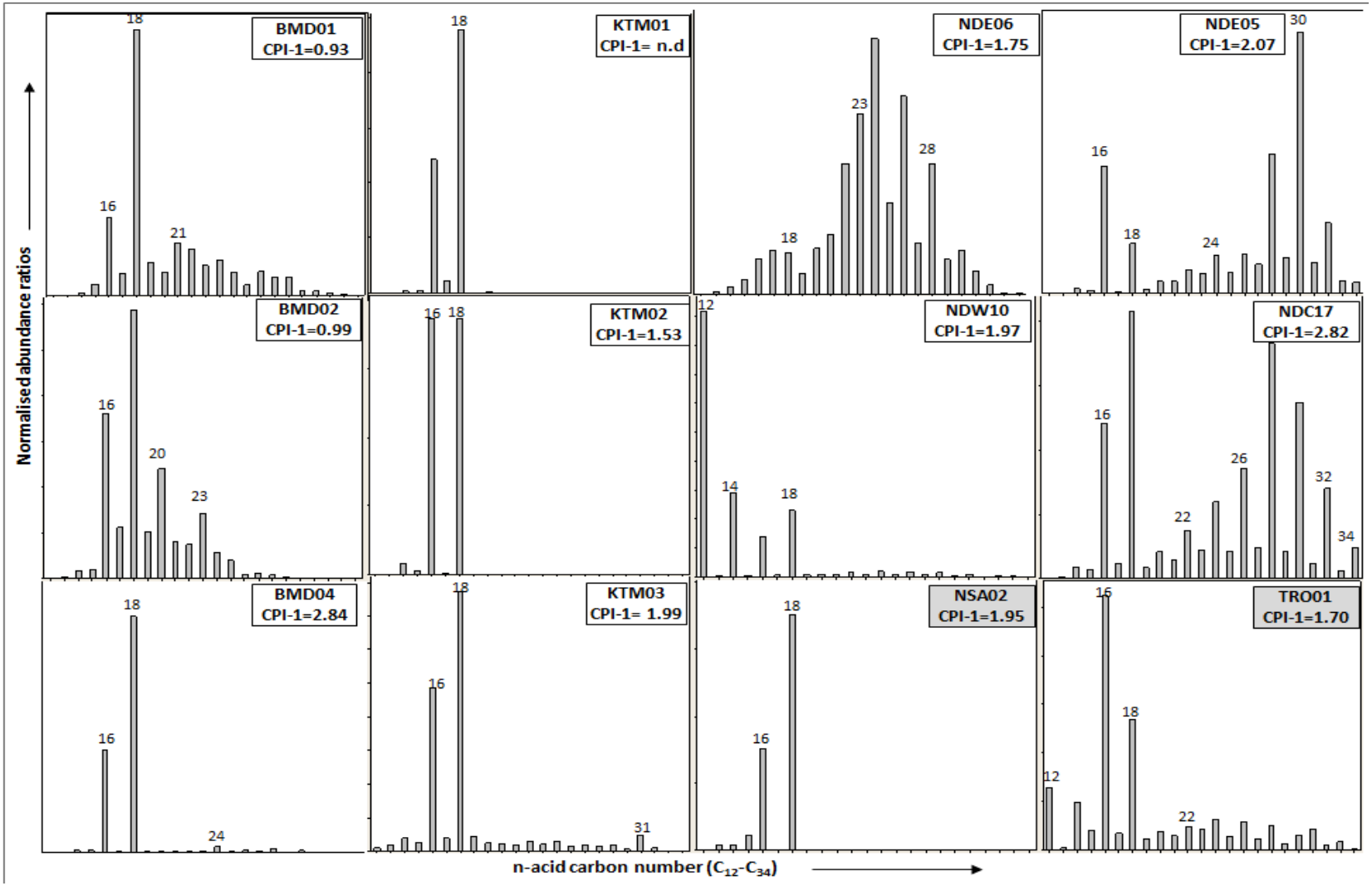
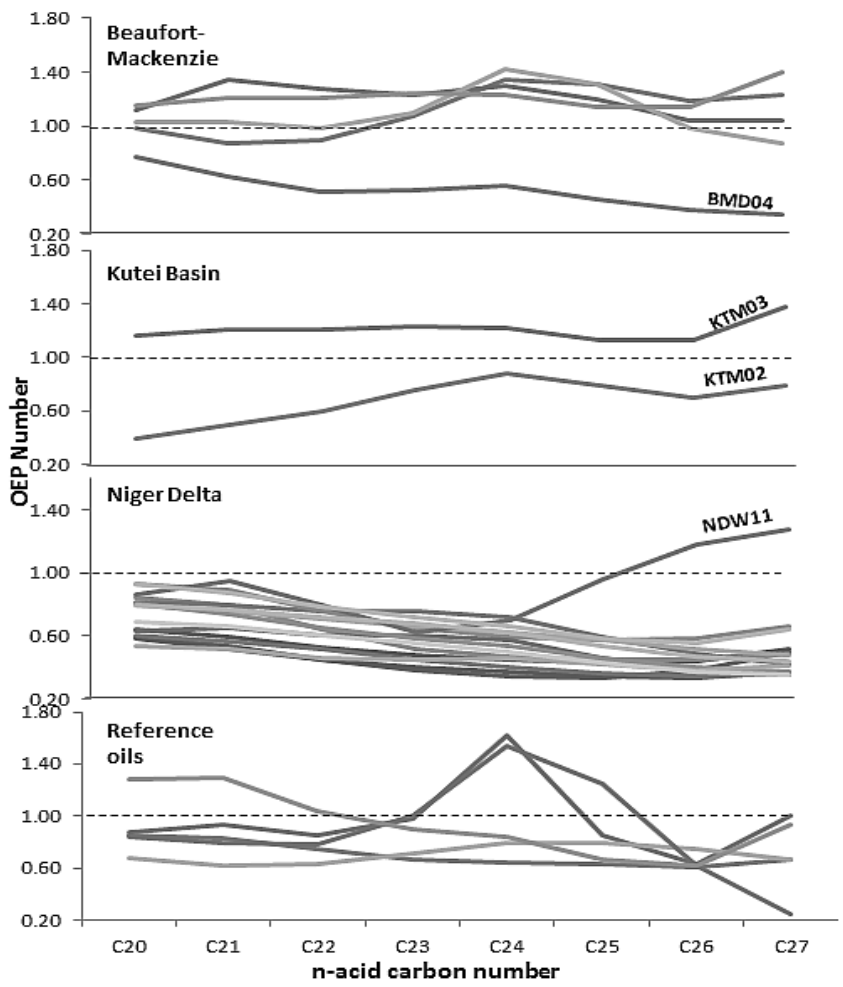


Figure 4.46 Distributions of *n*-acids in representative oils; Note the wide ranging maxima across samples and distribution differences between marine (e.g. NSA02), terrestrial (e.g. NDE06) and mixed (e.g. BMD01) oils. The peak numbers = *n*-carbon chain length of the acids. NSA02 and TRO01 are reference oils. CPI-1 = $(2\times C_{24})/(C_{23}+C_{25})$. Graphs are all on the same scale.



LCA OEP Numbers

Sample	n-C20	n-C21	n-C22	n-C23	n-C24	n-C25	n-C26	n-C27
BMD01	0.99	0.88	0.89	1.07	1.35	1.31	1.18	1.23
BMD02	1.12	1.34	1.28	1.23	1.29	1.20	1.04	1.04
BMD03	1.03	1.03	0.99	1.10	1.42	1.31	0.98	0.87
BMD04	0.77	0.63	0.51	0.53	0.56	0.45	0.37	0.35
BMD05	1.16	1.21	1.21	1.24	1.23	1.14	1.14	1.40
KTM02	0.39	0.50	0.60	0.75	0.88	0.79	0.70	0.78
KTM03	1.16	1.21	1.21	1.23	1.21	1.13	1.13	1.38
NDE01	0.60	0.53	0.45	0.38	0.34	0.34	0.39	0.50
NDE02	0.65	0.59	0.53	0.48	0.46	0.43	0.44	0.52
NDE03	0.84	0.79	0.64	0.52	0.47	0.45	0.45	0.49
NDE04	0.58	0.52	0.45	0.40	0.37	0.35	0.34	0.37
NDE05	0.82	0.80	0.76	0.76	0.72	0.60	0.49	0.42
NDE06	0.93	0.89	0.76	0.65	0.60	0.57	0.59	0.66
NDE08	0.60	0.57	0.52	0.45	0.40	0.36	0.35	0.37
NDW09	0.63	0.65	0.61	0.61	0.58	0.46	0.38	0.35
NDW10	0.80	0.76	0.70	0.66	0.62	0.57	0.52	0.48
NDW11	0.87	0.94	0.80	0.62	0.70	0.95	1.17	1.27
NDW12	0.81	0.73	0.65	0.59	0.53	0.46	0.40	0.38
NDW13	0.54	0.51	0.46	0.45	0.46	0.42	0.39	0.42
NDW14	0.93	0.88	0.79	0.72	0.66	0.59	0.55	0.64
NDW15	0.79	0.77	0.72	0.68	0.63	0.53	0.47	0.44
NDC17	0.69	0.66	0.61	0.55	0.50	0.43	0.38	0.36
TRO01	0.85	0.83	0.75	0.67	0.65	0.63	0.60	0.66
NSA02	0.88	0.93	0.85	0.98	1.62	0.85	0.63	1.01
NSA03	0.68	0.63	0.63	0.72	0.80	0.80	0.75	0.67
NSA04	0.84	0.80	0.78	1.00	1.54	1.25	0.62	0.25
NSV05	1.29	1.29	1.04	0.90	0.84	0.67	0.62	0.94

$$OEP_{number} = \left[\frac{(C_i + 6C_{i+2} + C_{i+4})}{(4C_{i+1} + 4C_{i+3})}\right]^{(-1)^{i+1}}$$

Figure 4.47 Plots of odd/even predominance (OEP) versus carbon number for crude oils from the 3case study Tertiary systems. The associated table shows the running OEP ratios for C_{20}-C_{27} *n*-acid carbon number which are derived from an improved carbon preference index (CPI) expression by Scalan and Smith (1970) as shown in the figure. 'C*i*'= relative amount of *n*-homologous series containing '*i*' carbons molecule; ratio incorporates 5 consecutive carbon chain length (*i*, *i*+1, *i*+2, *i*+3, & *i*+4) and centres around the '*i*+2' component. Odd or even carbon number predominates in acid fractions whose values are >1 or <1, respectively.

Two acyclic isoprenoid acids: pristanic (2,6,10,14-tetramethylpentadecanoic) and phytanic (3,7,11,15-tetramethylhexadecanoic) acids were also identified in most samples. Their abundances (Table 4.11) range widely from 0.4-21.5 ppm (Beaufort-Mackenzie), 2.6 - 12.9 ppm (Kutei Basin) and 5 - 66.5 ppm (Niger Delta). Quantitative data show that isoprenoid acids are in broadly similar abundances to the straight chain acids (Table 4.11). In many of the Niger Delta samples (NDE01,-02,-03,-05,-06, -08, and NDW11, -12 and-15), they, occur in concentrations equivalent to, or up to 2.5 times the abundances of C_{16} and C_{18} *n*-acids. Phytanic acid is more abundant than pristanic acids in all Niger Delta oils except NDW13. No prevalence of either of the isoprenoid acids was observed in the Beaufort-Mackenzie and Kutei oils. However both (Pr and Ph) acids generally vary correspondingly with abundances of linear acids. In terms of relative abundance, pristanic and phytanic acids are not applied in exactly the same interpretative way as their saturated alkane counterparts because the pristanic/phytanic acid ratios derived in this study (Table 4.11) do not correspond to those of pristane/phytane ratios. Even so, they could reflect the type of source organic matter, with values <1 reflecting predominantly terrestrial input while ratios >1 and up to 3 may suggest mixed oils of predominantly marine organic matter (cf. Seifert, 1975, Jaffé and Gallardo, 1993). Plots of pristanic/phytanic acid vs. pristane/phytane ratio for the case study oils (Figure 4.48) showed no clear linear relationship between both ratios but related oils are shown to be grouped together to some degree, in terms of their respective locations.

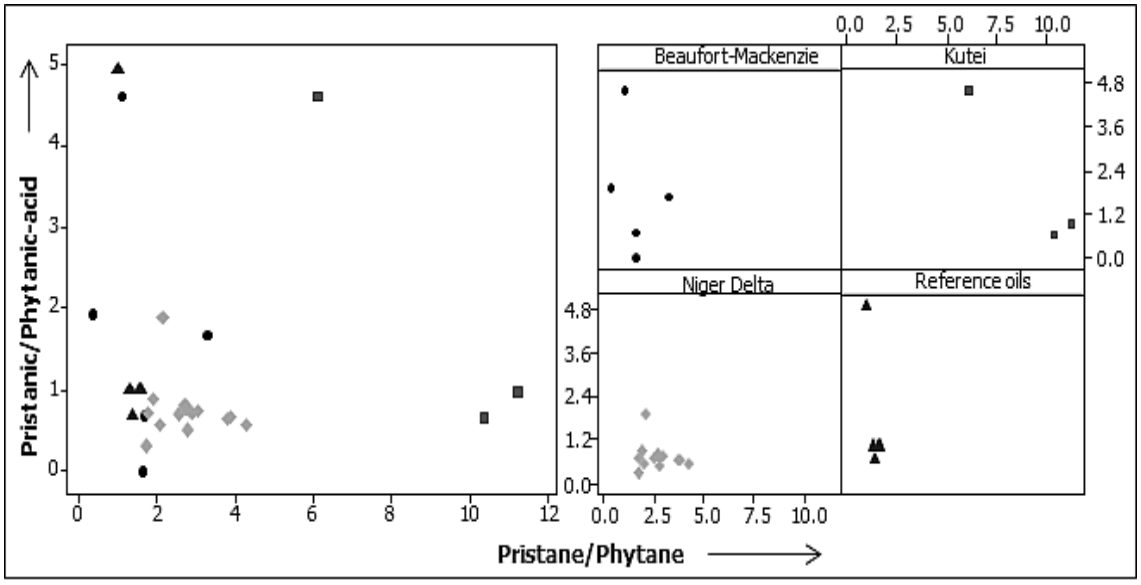


Figure 4.48 Plots showing the relationship between the pristanic/phytanic acid and pristane/phytane ratios in respective samples; the plots on the right show oils from individual areas on separate panels.

Odd-Even Predominance (OEP)

The OEP numbers and curves are derived to show the carbon number predominance using an improved CPI expression (Scalan and Smith, 1970). Because the OEP numbers derived in this manner are running ratios which, according to Scalan and Smith (1970) incorporate the amount of longer consecutive carbon chain length (≥5) of a homologous series, it can be distinguished from other CPI derivatives (e.g. Bray and Evans, 1961) and is adaptable as a correlation tool for assessment involving two or more characteristic homologous series containing i+2 carbon atoms in their molecules.

Figure 4.47 illustrates OEP curves for the long-chain (C_{20+}) *n*-acids of oils of individual sample subsets. In general, LCA with even carbon numbers predominate. These curves are very similar for the Niger-Delta oils suggesting a common origin. On the other hand, the dissimilarities in the OEP curves and mixed OEP values for Beaufort-Mackenzie and Kutei Basin oils suggesting various origins are expected for the former, but rather inconclusive for the latter due to the limited number of samples. Even-number carbon chain length distribution of fatty acids are typical of extracts from recent (immature) sediments (e.g. Cooper and Bray, 1963, Scalan and Smith, 1970), and since the alkane distributions are not similar to those of their fatty acid counterparts in most samples, it could be inferred that even predominance of *n*-acids in most oils is due to migration-derived acids.

4.8.2. *Hopanoic (Pentacyclic Triterpenoid) acids*

With respect to cyclic acids, only hopanoic acids were observed and quantified in the study samples. Hopanoic acids are relatively abundant and are thought to be the most widespread of crude oil acid components (Behar and Albrecht, 1984, Jaffé *et al.*, 1988b). Their detection was based on comparison with reported mass spectra and GC-MS mass chromatogram retention patterns (e.g. Schmitter *et al.*, 1978, Jaffé *et al.*, 1988b).

Typical isomeric distributions of C_{30}-C_{33} homologues of hopanoic acids identified in the study crude oils are shown in Figure 4.49. Most analysed oils in this study show the presence of hopanoic acids (HA) with highly variable isomer distributions (e.g. Figure 4.49; Table 4.12). Concentrations of HA varied within and across sample subsets, and ranged from below detection limits (~0.1 µg) up to 120 µg/g (total HA, Table 4.11). All four (C_{30}-C_{33}) homologues were widely distributed but the C_{32} components (32-HA, Table 4.12), often

followed by those of C_{31} (31-HA), dominated the distribution in most samples. C_{31} homologues were most abundant in only two samples (KTM02 and NDW15). The C_{30} and C_{33} HA were the least abundant in most samples and were absent in some samples. Both homologues are absent in KTM02 while ether one of both was not detected in BMD01, NDW15 and the reference oil, NSA02. Two of the Kutei Basin oils had no detectable hopanoic acids while KTM02 showed minor amounts of some C_{31} and C_{32} (ββ, αβ, and βα-22*R* only) HA.

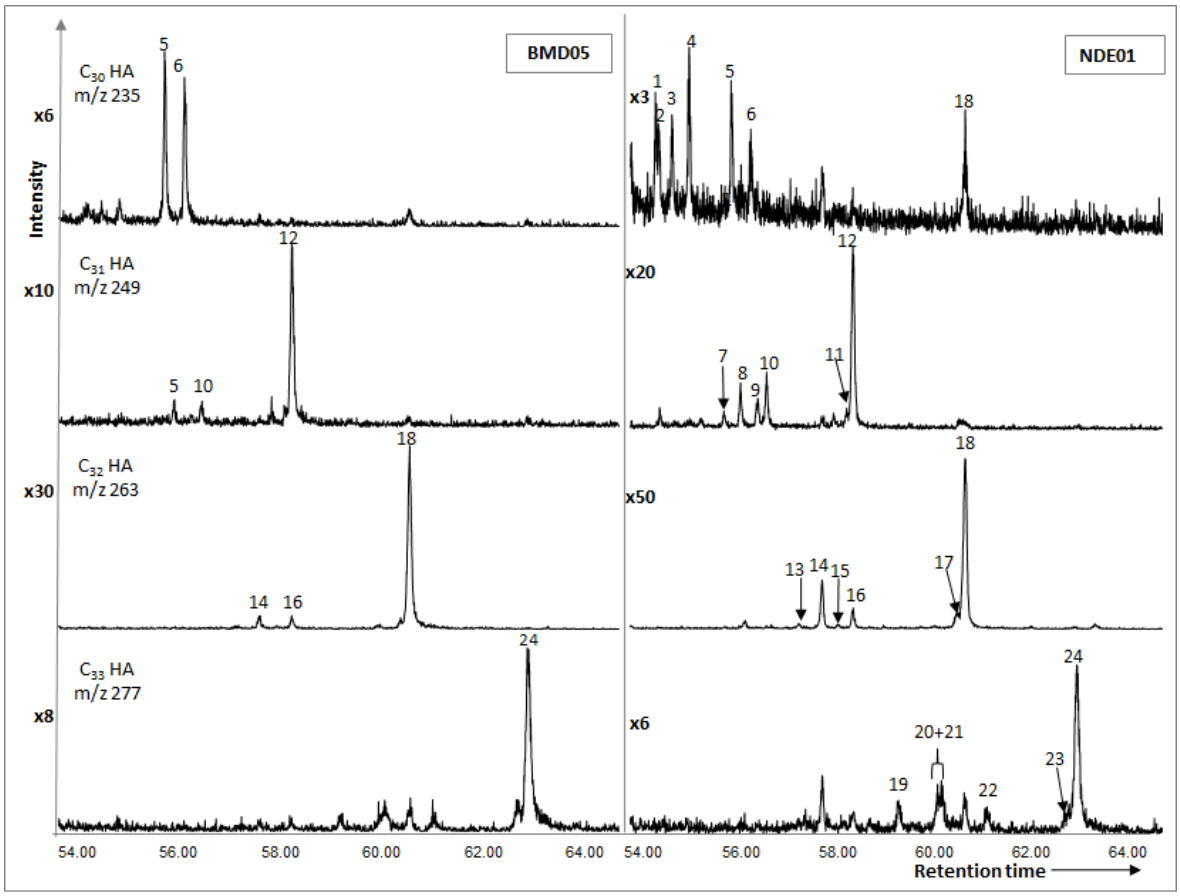


Figure 4.49 Mass chromatograms showing the C_{30} *(m/z* 235), C_{31} *(m/z* 249), C_{32} *(m/z* 263) and C_{33} (m/z 277) homologues of the hopanoic acids (as methyl esters) in selected oils: NDE01and BMD05; The 6 peaks denoted 1-6, 7-12, 13-18 and 19-24 are isomers of C_{30}-C_{33} HA, designated respectively as: 17α,2lβ,22*S*; 17α,21β,22*R*; 17β,21α,22*S*; 17β,21α,22*R*; 17β,21β,22*S* and 17β,21β,22*R* (after Jaffé *et al.*, 1988a). Note the predominance of C_{31} and C_{32} hopanoic acids. Intensity scale indicated on the y-axes are multiples of 1000; retention time is in minutes. A full list of the identified isomers is given in Appendix II-f.

The ββ isomers were dominant in most oils except NDW15 and NDC17 in which the more stable βα isomers dominate. The ββ isomers are the least mature and are thermally less stable than the αβ and βα 22*R* homologues (Jaffé and Gardinali, 1990). This low maturity signal in the acid fractions of mature, non-biodegraded oils is an indication of a secondary origin for the HAs in these oils.

Table 4.12 Hopanoic acid data showing the concentrations of C_{30}-C_{33} components identified in the study samples, as well as relevant molecular and isomeric ratios.

	30αβ	31αβ	32αβ	30βα	31βα	32βα	30ββ	31ββ	32ββ	30-HA	31-HA	32-HA	33-HA	HA				
Sample ID	Concentrations (ng/g)														**30αβR**	**31αβR**	**31βαR**	**32βαR**	**32ββ/αβ**
BMD01	997	465	613	737	985	1925	968	3103	6178	2702	4553	8716	n.d	15971	0.32	n.m	2.56	5.31	0.91
BMD02	n.d	203	534	230	328	200	461	1081	2377	691	1611	3111	1102	6515	n.m	n.m	n.m	n.m	0.82
BMD03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m
BMD04	363	n.d	811	n.d	n.d	n.d	389	1651	4046	752	1651	4858	1065	8326	0.51	n.m	n.m	n.m	0.83
BMD05	405	368	512	525	295	595	2466	2593	9905	3396	3256	11012	4379	22043	0.42	n.m	n.m	n.m	0.95
KTM01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m
KTM02	n.d	155	114	n.d	269	40	n.d	77	270	n.d	500	425	n.d	925	n.m	n.m	1.77	n.m	0.70
KTM03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m
NDE01	1602	2975	13414	2594	5843	6379	2001	16306	54671	6197	25124	74465	14328	120114	0.41	n.m	1.77	4.41	0.80
NDE02	768	1644	9264	1426	3042	2843	1769	10062	38435	3963	14748	50542	7514	76767	0.63	n.m	1.79	3.29	0.81
NDE03	432	761	1890	539	1217	1114	2095	3592	13542	3068	5570	16547	5248	30433	0.52	2.52	1.80	3.08	0.88
NDE04	350	1444	5992	945	1742	1710	1361	6492	30361	2656	9678	38062	6202	56598	1.00	1.91	2.32	10.48	0.84
NDE05	324	596	727	472	659	466	358	649	1396	1154	1905	2589	671	6319	0.38	1.49	1.23	3.57	0.66
NDE06	1075	1748	4063	1612	2318	1983	1870	4179	12568	4557	8246	18614	5234	36651	0.52	2.38	1.84	1.85	0.76
NDE08	826	2007	3383	1213	2831	2386	940	4781	15141	2980	9620	20910	4298	37808	n.m	4.54	1.27	2.81	0.82
NDW09	n.d	n.d	744	n.d	n.d	n.d	446	2334	2511	446	2334	3255	396	6431	n.m	n.m	n.m	n.m	0.77
NDW10	486	899	1933	838	1347	1138	902	1445	2512	2226	3691	5584	1391	12892	0.69	n.d	1.65	2.56	0.57
NDW11	1871	4802	6104	4404	7236	4460	3057	11587	20454	9331	23625	31018	9735	73709	0.52	2.30	1.52	4.04	0.77
NDW12	778	1704	2321	1308	1893	1174	1016	2260	2638	3103	5857	6133	1991	17084	0.47	2.68	1.78	3.89	0.53
NDW13	912	2022	3693	1974	3410	1947	3182	8980	26364	6069	14412	32004	6569	59054	0.56	1.79	1.95	5.10	0.88
NDW14	313	2125	3660	346	2786	1900	1442	6352	13535	2102	11263	19095	5308	37768	1.00	1.77	2.00	1.97	0.79
NDW15	1180	2070	1491	1097	2763	1154	n.d	986	513	2277	5819	3159	n.d	11255	n.d	1.79	1.54	2.93	0.26
NDC17	617	1425	2070	1153	2071	1183	n.d	1726	1435	1771	5223	4689	486	12169	0.51	2.80	2.18	6.04	0.41
TRO01	1242	2281	2642	1713	1843	1673	1647	2421	3989	4602	6544	8304	3005	22455	0.66	1.51	1.40	1.14	0.60
NSA02	n.d	n.d	n.d	n.d	n.d	n.d	n.d	2987	5280	n.d	2987	5280	1424	9691	n.m	n.m	n.m	n.m	1.00
NSA03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m
NSA04	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m
NSV05	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m	n.m	n.m	n.m	n.m	n.m

30αβ, 31αβ, and 32αβ = sum concentrations of 22*S*+22*R* epimers of individual C_{30}-C_{32}-17α(H), 21β(H)-hopanoic acids; 30βα, 31βα and 32βα = sum concentrations of S+R epimers of individual C_{30}-C_{32}-17β(H), 21α(H)-hopanoic acids; 30ββ, 31ββ and 32ββ = C_{30}-C_{32} (22*S*+22*R*)-17β(H), 21β(H)-hopanoic acids; 30-HA, 31-HA, 32-HA and 33-HA = sum concentrations of all detectable isomers of the C_{30}-C_{33}-hopanoic acid distributions in containing samples; HA = sum of all C_{30}-C_{33}-HA isomers; 30αβ*R*, 31αβ*R*, 31βα*R* and 32βα*R* are the *R/S* ratios of the αβ and βα isomers of indicated carbon components; 32ββ/αβ = C_{32}-(22*S*+*R*) (17β(H), 21β(H)-)/(17β(H), 21β(H)- + 17α(H), 21β(H)-HA); n.d/n.m = not detected or not measurable due to the absence of one or more components in the acidic fraction/ ratios. The shaded column indicate the representative reference oils containing at least one HA isomer. The greyed samples contained no detectable HA.

The 22*R* stereoisomer was more widespread and more abundant in relation to 22*S* throughout the sample set. The ββ *R/S* ratios (measurable only for those oils that contain both diastereoisomers) reflect the overwhelming dominance of the *R*- over the *S*- stereoisomer, especially for the C_{31}-C_{33} homologues whose ratios range from 10.41-20.97, 10.73-25.49, and 2.40-9.11, respectively (Table 4.13). Again these ratios are highest for the C_{32} homologues of the oils studied. The αβ and βα *R/S* ratios of C_{31}-C_{33} homologues are not measurable for the Beaufort-Mackenzie oils due to the absence of the corresponding '*S*' stereoisomer in these samples. However, they range from 1.49-4.54 and 3.00-15.72 for the αβ-C_{31} and C_{32} isomers and 0.92-4.83, 1.23-2.56 and 1.14-10.48 for the C_{30}-C_{32} βα isomers, respectively, in the Niger Delta oils (Table 4.13). In general, the *R/S* ratios of the αβ and βα isomers for C_{31} and C_{32} are greater than those of C_{30} homologues. This observation contrasts with the findings of Jaffé *et al.* (1988a) in which the C_{30} *R/S* ratios are higher than those of C_{31} and C_{32} homologues. The αβ and βα *R/S* ratios are indicators of the integration of immature OM into the oils based on the concentrations and occurrences of both pairs of diastereoisomers.

Table 4.13 Epimer ratios (22*R*/22*S*) of Hopanoic acid isomers.

Isomers	ββ-(22R/22S)				αβ-(22R/22S)				βα-(22R/22S)			
Sample ID	C30	C31	C32	C33	C30	C31	C32	C33	C30	C31	C32	C33
BMD01	0.95	11.88	20.30	n.m	0.47	n.m	n.m	n.m	2.72	2.56	5.31	n.m
BMD02	0.87	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
BMD03	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
BMD04	n.m	n.m	n.m	n.m	1.03	n.m	n.m	n.m	n.m	n.m	n.m	n.m
BMD05	0.47	17.93	24.86	8.77	0.72	n.m	n.m	n.m	1.76	n.m	n.m	0.64
KTM01	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
KTM02	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	1.77	n.m	n.m
KTM03	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NDE01	0.78	11.99	10.73	7.45	0.70	n.m	7.82	1.40	1.99	1.77	4.41	0.53
NDE02	0.74	20.97	11.79	8.33	1.69	n.m	15.72	2.19	0.92	1.79	3.29	0.74
NDE03	0.68	13.25	17.47	6.93	1.08	2.52	4.11	1.35	1.75	1.80	3.08	0.99
NDE04	0.71	17.66	15.05	8.35	n.m	1.91	9.17	0.95	4.83	2.32	10.48	0.51
NDE05	1.25	n.m	15.05	n.m	0.60	1.49	6.06	n.m	1.68	1.23	3.57	0.34
NDE06	0.61	15.99	15.67	5.22	1.08	2.38	3.93	1.13	1.15	1.84	1.85	0.70
NDE08	0.65	n.m	n.m	n.m	n.m	4.54	5.70	3.19	1.30	1.27	2.81	n.m
NDW09	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NDW10	0.75	n.m	n.m	n.m	2.18	n.m	4.43	1.32	2.09	1.65	2.56	n.m
NDW11	0.57	n.m	22.32	5.84	1.10	2.30	4.34	0.00	1.08	1.52	4.04	0.58
NDW12	0.54	10.41	n.m	2.40	0.90	2.68	3.77	2.89	0.96	1.78	3.89	1.81
NDW13	0.70	n.m	21.30	9.11	1.26	1.79	10.95	1.20	1.50	1.95	5.10	0.72
NDW14	n.m	17.05	25.49	7.53	n.m	1.77	3.64	0.81	n.m	2.00	1.97	n.m
NDW15	n.m	n.m	n.m	n.m	n.m	1.79	3.00	n.m	1.27	1.54	2.93	n.m
NDC17	n.m	n.m	n.m	n.m	1.04	2.80	3.72	0.00	1.36	2.18	6.04	n.m
TRO01	0.88	n.m	n.m	7.80	1.92	1.51	2.53	1.91	0.94	1.40	1.14	n.m
NSA02	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NSA03	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NSA04	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m
NSV05	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m	n.m

All ββ-, αβ- and βα-HA isomer were all identified in the samples at varying levels. The ββ isomer is the least mature and most abundant in the oils. n.m means not measureable to absence or low concentration of one or both epimers. CAN06, CAN07, CAN08, NDE07 and NDC16 were not analysed for acids in the first instance due to insufficient samples, and so no acid data is shown for these samples. The greyed samples are the reference oils.

No HA were detected in the reference (Jurassic, Type II North Sea) oils (NSA03, NSA04 and NSV05; Table 4.11). These oils are regarded as typical mature oils which have probably not migrated through immature sediments and hence, were not subject to migration-contamination (Jaffé and Gallardo, 1993). However, two other reference oils (TRO01 and NSA02) contain up to 22 µg/g total HA. They have also shown attributes of oils with significant terrestrial OM input throughout this investigation by their comparable geochemical characteristics to those of the case study oils (e.g. Table 4.3, Table 4.6).

4.9. Summary

4.9.1. *Geochemical Characteristics of Oil samples*

All 33 samples, consisting of three subsets of case study oils and a fourth subset, which includes a Trinidad oil and four reference Jurassic marine Type II North Sea oils, were investigated. Bulk geochemical data (Table 4.2, Table 4.3, and Table 4.4) from the aliphatic and aromatic hydrocarbons of the sample set have shown the oils to be, at least, early to mid-mature. The distributions of triterpanes and steranes were applied to evaluate the thermal maturity, source facies, kerogen type, lithology and depositional environment of the oil source rocks.

The Beaufort-Mackenzie Delta oils, separate into two groups: those sourced from kerogen with higher plant organic matter input and the other group sourced from predominantly marine kerogen with high algal input. The marine oils (BMD01, BMD03, BMD04 and BMD05) are thought of as being sourced from below the Tertiary delta but had migrated into the upper sequences and are reservoired alongside the other Tertiary sourced oils within the Tertiary deltaic reservoirs in the Beaufort-Mackenzie Delta (e.g. Brooks, 1986a, Curiale, 1991). Many of these oils including BMD01, BMD02, CAN07 and CAN08, however, have been shown to be severely biodegraded (Table 4.1; Appendix III-c).

Oils of the Niger Delta in this study are classed into two end-member groups and possibly, an intermediate group. Most North-Eastern, central and some of the North-Western Tertiary oils of the delta are characterised as having high inputs of terrigenous organic matter to their source rocks. Some of the North-Western oils (e.g. NDW09, NDW10) have mixed marine and terrigenous organic matter source signatures, a reflection of mixed accumulations and possible co-sourcing from pro-delta shales (c.f. Samuel et al., 2009). Although limited by the number of available samples, the interpretation of data on three studied oils of the Kutei Basin revealed similarities in their hydrocarbon compositions and particularly in their

biomarkers. They possessed the characteristics of intra-delta oils derived from Tertiary coaly shales with abundant higher plants input. The Jurassic North Sea marine-sourced 'reference' oils were chosen, for comparison with the case study Tertiary oils, especially relating to their olefin and carboxylic acid contents. TRO02, as well as NSA02, were also chosen as reference oils for their molecular and source similarities with the case study samples while at the same time possessing the attributes of marine-sourced oils. Data from their analysis is expected to compare to those of like for like case study oils mainly for the purpose of testing the study hypothesis.

4.9.2. *Olefins and Implications of their Occurrence*

Although the concentrations of olefins were generally low and varying in composition throughout the sample set, their presence and distributions in oils that had clearly attained oil generation thermal maturity would suggest a secondary origin in most of the samples. It has also been shown by review of petroleum systems of the study oils, that they could have been generated from mature source rocks within the Tertiary sequence, and migrated and accumulated up into the Tertiary reservoirs there, or have been derived from older source rocks lying below the Tertiary sequences through which migration took place post-expulsion. Thus, although the study oils were reservoired in the Tertiary sands of their respective deltas, their sources may differ even for oils of the same basin, and also the oils might have migrated through thermally immature, organic-rich sediments. The olefins detected in these samples therefore could be both source- and migration-derived.

The occurrence of oleanenes was shown to be prominent in Tertiary oils and/or those containing relatively high amounts of oleanane, but they were in very low abundance or absent in the other Paleogene/Cretaceous oils analysed. The correlations observed between the oleanene isomers and urs-12-ene (Figure 4.36) in case study samples, suggest that the oleanenes found in the Beaufort-Mackenzie oils are indigenous to them and are not derived due to migration. This is because the oleanene isomers would not have exhibited such correspondence if they were merely picked up along the oil migration path. Furthermore, oleanenes found in many Tertiary oils have been reported as source-derived olefins mainly due to their proposed thermal stability and presence at relative maturity (e.g. Curiale, 1995, Eneogwe *et al.*, 2002). In the case of the Niger-Delta Basin, it seems likely that a portion of the oleanenes in most of its studied oils could have been picked up at some point during migration. This deduction is based on the observed lack of correlation between oleanene isomers (Figure 4.36), and the total oleanenes vs. oleananes (Figure 4.35); a reflection of the

oleanenes being collectively source- and migration-derived. A review of the Kutei Basin petroleum systems revealed a complex history in the generation, expulsion, migration and the entrapment of these oils in the most prevalent Tertiary reservoirs. Analyses of the oils revealed the presence of terrigenous biomarkers including oleanenes and oleanane. However, the total concentration of olefins detected in these samples were the lowest of all Tertiary oils in the sample set. Therefore, it is difficult to determine if the overall molecular make-up of these oils is truly source-defined or migration-defined, but the likelihood of migration-induced compositional changes still remains, and needs to be addressed. Although limited in number, the distribution of the biomarker compounds in the Kutei condensate samples, especially with the dominance of the lower carbon homologues over the high molecular weight ones in almost all classes of compounds observed, has shown that these oils may have suffered the effects of migration-fractionation (Curiale *et al.*, 2005). Their physical properties (e.g. clear, light oil), high parafinicity with abundant light hydrocarbons and very low abundance or absence of high molecular weight ($>C_{26}$) hydrocarbons (e.g. Table 4.2, Table 4.3) are suggestive of hydrocarbons that may have been separated from the residual oil following a pressure drop due to long-range vertical migration (occurring up along fault zones) of a single phase petroleum to the subsurface (Curiale and Bromley, 1996b).

Although oleanenes and ursenes identified in most oils could have been derived directly from the source rock, other olefins found in many of these oils were considered to have been dissolved from thermally immature, non-source, organic-rich rocks during migration as implied by a number of factors including: the non-correspondence of C_{14}-C_{26} carbon number *n*-alkene homologues, to those of the *n*-alkanes; the difference in the carbon preference indices (CPI) and odd/even predominance (OEP) numbers in the linear alkene and alkane homologues of most samples; and the presence of other olefins such as diasterenes and hopenes (Figure 4.22) characteristic of immature organic matter. All these olefins are unlikely to have survived the oil generation temperatures, and therefore, the migration-contamination hypothesis is very likely for these oils.

4.9.3. *Carboxylic Acids as Indicators of Migration-Contamination*

It has been shown that carboxylic acid contents are high in immature sediments but typically minimal in newly generated mature crude oils, and consist mainly of short-chain acids (Jaffé and Gardinali, 1990). Molecular distributions of carboxylic acids in crude oils have also been shown to be controlled by oil migration and geochromatography and, to a lesser extent,

naturally occurring acids (SCA) in the oil upon generation (Jaffé *et al.*, 1988a). While the distributions of the hopanoic acids (HA) can be altered by incorporation of organic matter to the original oil, geochromatographic effects on the acids are mainly determined by the differences in polarity of the acids (e.g. linear SCA and LCA). Both of these processes will affect the HA maturity parameters and the relative abundances of LCA to SCA (C_{28}/C_{18}) respectively (Jaffé *et al.*, 1988b).

In samples of marine origin (e.g. NSA02; Figure 4.46), where acids are present, a strong preference of short-chain acids (SCA, C_{12}-C_{19}) compared to long-chain acids (LCA, C_{20}+) was observed. This preference is weak, and less prominent in the oils of terrestrial origin (e.g. BMD02, KTM03, and NDE06), which are distinguished by their relatively higher LCA content. The mixed oils (e.g. BMD01, NDE05, and TRO01) showed intermediate distribution between the marine and terrestrial oil groups. High carbon preference indices (CPI) of the short-chain *n*-acids are expected since the dominant acids in most samples were C_{16} and C_{18} (Figure 4.46). All saturated fatty acids have a marked even over odd carbon number predominance (<1). The low abundance or absence of carboxylic acids in non-biodegraded Jurassic marine reference oils distinguishes them from those of the non-marine oils in the sample set.

In the Niger Delta oils, the low maturity signature by the more prevalent immature 17β(H),21β(H) hopanoic acid isomers relative to the more mature 17α(H),21β(H) and 17β(H),21α(H) isomers is probably due to the solubilisation of these acid components by the migrating oils. It seems that the presence of least mature ββ isomers does not correspond with maturity in the oils, or have not altered distributions of hydrocarbon biomarkers (i.e. terpanes and steranes) in the oils that have them. One possible explanation for this is that if the oils originally had negligible concentrations of HA, if they then picked up even very low (ppm) concentrations of these acids during migration, then the migration-derived HA would then dominate the resulting oil HA distribution. However, if the original oil had very high concentrations of other hydrocarbon biomarkers, then if it picked up a very low or negligible amounts of the HA relative to those of the other biomarkers during migration, then the migration-derived acid biomarkers may not greatly affect the resulting oil hydrocarbon biomarker distributions. Even-numbered carbon chain lengths predominate in typical fatty acids and straight chain olefin distributions of the study oils as opposed to a typical non-predominance (OEP ≈ unity) or odd predominance of the *n*-alkanes. The similarity of the OEP curves for the acids suggests a common origin (e.g. Scalan and Smith, 1970) as shown in Figure 4.28 and Figure 4.47.

4.9.4. *Relationship between Olefins and Carboxylic Acids in Crude oil*

Both acylic and cyclic types of olefins and carboxylic acids were identified and quantified. Highly variable isomer distributions (HA), as well as wide-ranging differences in concentrations of both classes of compounds in the study oils were observed. The olefins varied proportionally with the abundances of HA in most samples. Summed concentrations of olefins (up to ~600 ppm) were much lower than those of the acids (up to ~6000 ppm). However, there was no clear relationship between the concentrations of *n*-acids and *n*-alkenes, total olefins and total acids, total *n*-alkenes and *n*-alkanes, and total HA and corresponding hopanes (Figure 4.50).

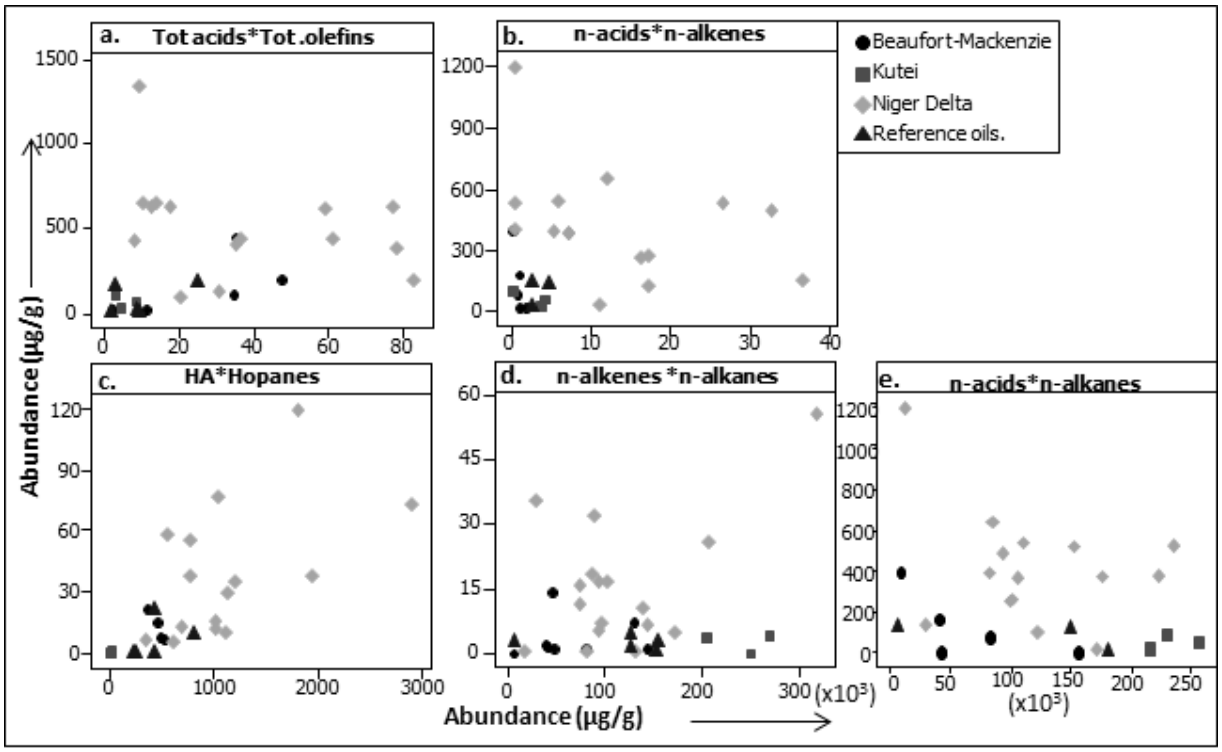


Figure 4.50 Cross plots of (a) total acids (y-axis) vs. total olefins (x-axis); (b) total (C_{12}-C_{34}) *n*-acids (y-axis) vs. total (C_{12}-C_{26}) *n*-alkenes (x-axis); (c) Total HA (y-axis) vs. sum (C_{30}-C_{33}) hopanes (x-axis); (d) C_{12}-C_{26} *n*-alkenes (y-axis) vs. *n*-alkanes (x-axis); and (e) total *n*-acids (y-axis) vs. total *n*-alkanes (C_{12}-C_{36}) (x-axis), showing relationship between them. No distinct correlation is observed in plots a, b, d and e; but a weak positive correlation is displayed by the hopanoids (c).

The present study confirms that low amounts of both olefins and carboxylic acids may be present in non-biodegraded oils, but their relatively high abundance in certain oils, especially Tertiary deltaic oils, are strong indications of migration-induced alteration. In order to address questions about the origin of these unlikely components in certain geological samples, esp. thermally mature and non-biodegraded oils, attempts were made to establish relationship between olefins and acids in the oils, but no conclusive correlations were observed (e.g. Figure 4.50). This could be due to compositional variations in the immature organic-rich beds through which the oils have migrated.

Chapter 5 Laboratory Oil Migration Study

5.0.Introduction

An oil migration simulation experiment was set up and carried out in the laboratory to ascertain the extent to which biomarker signatures of produced oils can be changed by migration-contamination. Here a medium gravity, mature, non-biodegraded North Sea oil (NSA03) represented the migrating oil, while ground organic-rich, immature Kimmeridge Clay formation mudstone, sampled from Dorset, UK, represented the solid phase through which the oil was migrated. The solid particles are classed into three different mesh sizes: 4mm-1mm, 1mm-63µm and <63µm; the particles themselves, their extracts, and related artificially migrated samples, will be assigned notations corresponding to 'course', 'medium', and 'fine', respectively, throughout this chapter. The artificial migration system was constructed using high performance liquid chromatography (HPLC) stainless steel column connected to a pressure pump. Aliquots of the oil were pumped through the mudstone-packed column and collected as 'migrated' eluates. The composition of the Kimmeridge rock extracts and the North Sea oil were assessed prior to, and after the experiment. The analytical procedures used in this part-study for the olefin, carboxylic acid and hydrocarbon analyses were the same as those employed in the field sample study. These have been previously described in detail in the methodology chapter.

5.1.Approach: Brief Review

Migration of oils through porous media has been shown to produce changes in composition at both bulk and molecular levels (Bonilla and Engel, 1988, Zhusheng *et al.*, 1988, Brothers *et al.*, 1991). Laboratory simulation of this process has to be carried out under conditions that limit the time and magnitude of such processes as compared to those that occur in nature. Such limitations tend to magnify the effects created by simulation experiments over those supported by field observations (Trindade and Brassell, 1992). Given the complexity of the processes that affect the chemical makeup of petroleums in their original sedimentary settings, it is often difficult to assess these changes in natural samples that are, themselves, migrated oils (Bonilla and Engel, 1986). Hence this work uses a laboratory simulated migration technique which is similar in part, to the works of Bonilla and Engel (1988), Brothers *et al.* (1991), Krooss *et al.* (1991), Leythaeuser *et al.* (1984) and Zhusheng *et al.* (1988), but may offer an improved understanding of migration effects on oil composition through focussing on different compound classes as potential oil migration-contamination markers. The main focus of the approach is to establish compositional and distributional

changes in olefins and acids in migrated oils, in combination with conventional hydrocarbon based parameters.

5.2.Results and Discussion

Prior to the simulated migration experiment, the oil and rock samples used were initially characterized using a number of analytical techniques, such as solvent extraction (Table 5.1), TOC analysis, Rock-Eval pyrolysis (Table 5.2), hydrocarbon and carboxylic acid analysis (SAX/SPE), GC, and GC-MS, as described in Chapter 3.

5.2.1. *Rock Sample Data*

Solvent Extract Yields

The solvent (Soxhlet) extractable organic matter (EOM) yields for the different rock size fractions are shown in Table 5.1, as well as the yields normalised to total organic carbon (CNE-carbon normalized extract). The extract yields ranged from 25-30.67 mg/g rock which was highest in the 1 mm-63 µm particles and lowest in the finest particles. These values also correspond to the CNE measurements (56.43-57.84 mg/g). CNE is the total amount of extract, expressed as ppm of rock, or normalized to the organic carbon content, usually as mg extract/g rock.

Table 5.1 Yield of solvent extractable organic matter from different size fractions of the Kimmeridge rock.

	Extract Yield		
Particle size	4mm-1mm (Coarse)	1mm-63µm (Medium)	<63µm (Fine)
Sample Wt. (g)	40	30	20
Extract Wt. (mg)	1200	920	500
Extract/rock (mg/g)	30.00	30.67	25.00
CNE (mg Extr/g TOC)	57.84	61.36	56.43

Data was derived from solvent extraction and TOC analysis data. CNE = Extract yield / TOC content, is a normalised measurement of the extractable organic matter relative to TOC. The CNE measurement was adapted from pIGI extract yield analysis.

Pyrolysis Yields

Replicate data of Rock-Eval pyrolysis and total organic carbon (TOC) analyses for the three size fractions of the Kimmeridge mudstone sample used in this study are presented in Table 5.2. The TOC content is in the range 44.3-52.6%, and varies inversely with the particle sizes.

The measured TOC and Rock-Eval pyrolysis values are similar to those reported by Barth and Bjorlykke (1993) for similar Kimmeridge Clay samples from the same area.

Table 5.2 Data showing replicate measurements and derived parameters from the Rock-Eval pyrolysis of the three particle fractions of the Kimmeridge Clay.

Pyrolysis data						
	Rep1			Rep2		
Sample	Coarse	Medium	Fine	Coarse	Medium	Fine
Particle size	4mm-1mm	1mm-63µm	<63µm	4mm-1mm	1mm-63µm	<63µm
Sample wt. (g)	18.4	18.6	18.7	18.5	17.6	19.1
TOC(%)	51.87	49.98	44.3	52.62	50.08	44.85
T_{max}	419	421	418	421	419	417
S_0 (Gas)	0.05	0.05	0.21	0.10	n.d	n.d
S_1 (mg Oil/ g rock)	9.51	8.27	8.93	7.56	7.38	8.32
S_2 (mg/g rock)	333.15	326.45	340.53	318.91	288.18	283.35
HCGP = (S_1+S_2, mg/g)	342.66	334.72	349.46	326.47	295.56	291.67
PI = S_1/(S_1+S_2)	0.028	0.025	0.026	0.023	0.025	0.029
HI = (S_2/TOC)*100	642	620	681	637	651	632

Total organic carbon (TOC) = wt. % organic carbon in the rock; T_{max} = temperature at which the S_2 peak is maximum; S_0 and S_1 = first recorded peaks of fluid hydrocarbons released during programmed heating at low temperature (~300ºC); S_2 = second peak denoting evolved hydrocarbons by programmed cracking of sample kerogen from 300ºC up to 550°C; hydrocarbon generation potential (HCGP) = (S_0+S_1+S_2); hydrogen index, HI = S_2 normalized to the TOC (S_2*100/TOC); Production Index (PI) = S1/(S1+S2) (Peters, 1986, Langford and Blanc-Valleron, 1990).

Values of T_{max} obtained from Rock Eval analysis are between 417ºC and 421ºC (Table 5.1) which characterises the organic matter as thermally immature (Espitalié *et al.*, 1985). This low maturity level is also indicated by the low range values (0.023-0.029) of derived production indices (PI) across the three size samples. Based on the Rock-Eval data and graphical correlation of some parameters (direct and/or derived), the Kimmeridge Clay kerogen is characterised as Type II (Figure 5.1).

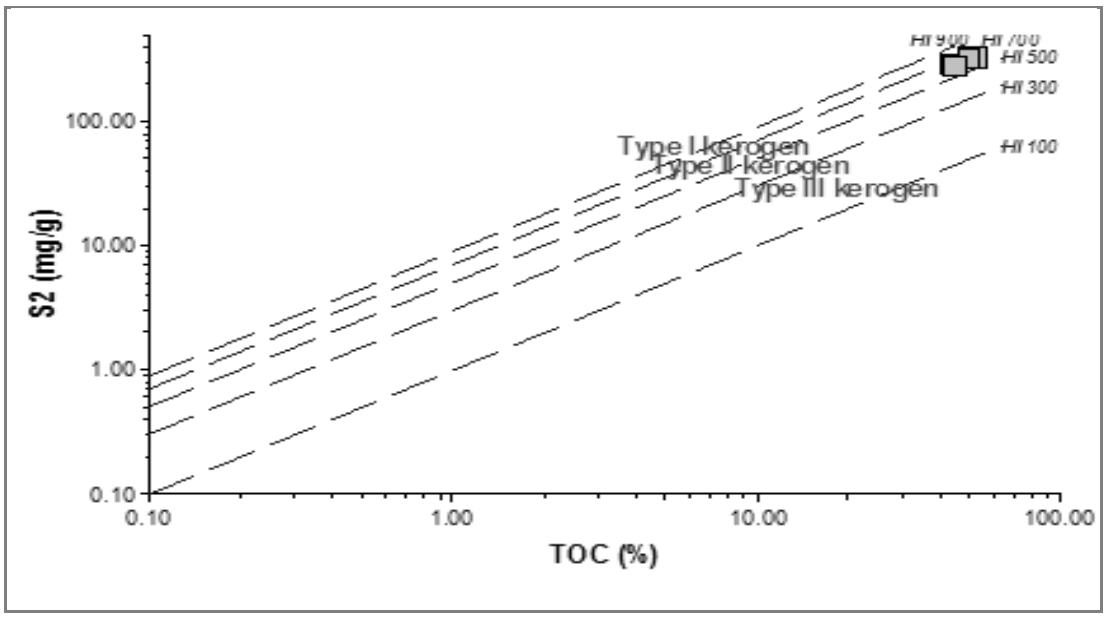


Figure 5.1 Log S_2 (mg/g rock) versus LogTOC (%) diagram showing the relationship between both parameters and the kerogen type. Overlays derived from pIGI geochemical analysis software.

BET Surface Area

The results of the Brunauer-Emmett-Teller (BET) analysis, for surface area determination of the three particle-size fractions, are shown in Table 5.3. The obtained BET specific and BET total surface areas vary widely across the three fractions. This variation is more prominent in latter calculated values and could be due to variations in both sample weight and particle size in the sample tube. The free space is measured by the instrument during the analysis and can be perceived to increase with decreasing particle sizes of the crushed sample. The large differences between the weights of the three different sized particles ('e', Table 5.3) that filled sample tubes of same volume correspond directly to differences in the void volume created by these sample variants in the tubes. Therefore the BET total surface area is controlled by free space (void) volume in the packed sample tube. The accuracy of these results is not conclusive due to the working condition of the analyser, which had just undergone major maintenance at the time of this analysis. Instrument display and derived values are considered as estimates mainly for the purpose of data comparison and deduction.

Table 5.3 Measurements taken during sample pre-treatment, and the surface area analysis of rock particles using liquid nitrogen @ 77K.

	Sample Tube	Tube 1	Tube 2	Tube 3
a	Particle size	Coarse (4mm-1mm)	Medium (1mm-63µm)	Fine (<63µm)
b	Wt. of raw sample + tube (g)	26.1081	17.8296	17.3546
c	Wt. of tube + outgassed sample (g)	26.0358	17.805	17.344
d	Wt. of sample tube assembly (g)	21.2219	16.4655	16.7316
e	raw sample wt. (g)	4.8862	1.3641	0.623
f	Wt. of outgassed sample (g)	4.8139	1.3395	0.6124
g	% impurities	1.48	1.80	1.70
h	BET (Specific surface) Area (m^2 /g)	4.467	4.400	9.625
i	Calc. total surface (BET) area (m^2)	21.5037	5.8938	5.8944

'd' = weight of empty sample tube; 'e' = initial wt. of sample prior to pre-treatment and analysis; 'f' = weight of 'pure' sample; 'g' = (('e'-'f')/'e')*100; 'h' = the instrument display BET (specific surface) areas, per gram of sample; and 'i' is derived from 'h' and is seen to be affected by sample weight, sample packing and free space volume.

Pore Size Distribution (Porosity) and Particle Density

The pore size or volume and their distributions in the Kimmeridge Clay samples were determined using the mercury intrusion cell porosimetry (MICP) procedure. Table 5.4 shows the measurements given by the instruments from which other parameters were derived. The intrusion volumes of the mercury, meant to fill pores of varying volumes at every pressure increment, are measured. The range of apparent diameters of pores for which this test method is applicable is fixed by the operating pressure range of the testing instrument. The range of these external pore-entrance diameters, applied in the present procedure is about 0.005-75 µm (Table 5.4). The pore radii or diameters, cumulative pore volume and cumulative porosity are also recorded at the same time during the analysis. The technique allows the use of these data readings, with other sample preparatory measurements (e.g. penetrometer volume, sample volume, mercury density etc.), to calculate useful parameters such as sample bulk density, mean pore radius, and total porosity. Since mercury intrusion porosimetry only measures external pores of rock fragment (Cook and Hover, 1999), a measure of the total porosity which includes those pores outside and within the sample particle could be obtained using the bulk density of the 'unintruded' sample.

Table 5.4 MICP analysis data showing the pore volumes and their distributions within the porous clay particles.

MICP Analysis Data/Result							
Date	21/05/2012	Sample Depth (m):	n/a	Pen. Vol. (ml)	6.05685	Sample Volume (ml)	0.8375
Instrument	Penetrometer	Sample Weight (g)	1.1383	Sample + Pen. Wt. (g)	63.7464	Total Porosity	0.0890
Pen. #/ Type	07-0002/5cc Solid	Corrected Vol. (ml)	0.8310	Sample + Pen + Hg wt. (g)	134.4161	Corrected porosity	0.0819
Run Set #	1	Sample bulk Density(g/ml)	1.3592	Hg weight (g)	70.6697	Mean pore radius (nm)	7.7596
Sample	KCF BlackStone	Corrected Density g/ml)	1.3698	Hg Density	13.5399	Particle density, Gs (g/ml)	1.492

Pressure (psi)	Cum. pore Vol.(ml/g)	Pore Diameter (µm)	Intrusion (micron ml)	Pore radius (nm)	Cumulative porosity	Corrected distribution	mean pore radius (nm)	Density distribution	%Cumulative distribution	rmean (nm)
3	0.0018	72.8895	0.002049	36444.7	0.086576					
5	0.0028	43.7337	0.003187	21866.8	0.085217		28229.982	0.006127		
7	0.0032	31.2384	0.003643	15619.2	0.084673		18480.874	0.003721		
10	0.0037	21.8668	0.004212	10933.4	0.083994		13067.936	0.004387		
14	0.0043	15.6192	0.004895	7809.6	0.083178		9240.4264	0.005581		
18	0.0045	12.1482	0.005122	6074.1	0.082906		6887.4009	0.002491		
25	0.005	8.7467	0.0056915	4373.3	0.082227		5154.0436	0.004763		
40	0.005	5.4667	0.0056915	2733.3	0.082227		3457.4407	0		
60	0.0052	3.6445	0.005919	1822.2	0.081955		2231.7811	0.001544		
100	0.0053	2.1867	0.006033	1093.3	0.081819		1411.5088	0.000613		
150	0.0057	1.4578	0.006488	728.9	0.081275		892.71654	0.003087		
200	0.0057	1.0933	0.006488	546.6	0.081275		631.23148	0		
300	0.0057	0.7289	0.006488	364.4	0.081275		446.34806	0		
400	0.0057	0.5467	0.006488	273.3	0.081275		315.63018	0		
550	0.0057	0.3976	0.006488	198.8	0.081275	0.08191	233.11366	0	100	7.7596

Range of apparent diameters of pores (0.005- ~73µm) is fixed by the operating pressure range (3-3900psi) of the test instrument. This table is a partial presentation to show relevant information. The full table of data is shown in Appendix VI-c for migration experiment data. Total Porosity = 1 - (bulk density/particle density); Sample bulk density = sample wt. /sample volume; sample volume = penetrometer volume - (Hg wt. /Hg density); Hg = Mercury (intruding liquid); intrusion volume = cumulative pore volume x sample wt.; corrected volume = sample volume – intrusion volume at 100% cell penetration.

Particle density (mg/ml) was determined using the pycnometer method (specific gravity bottle); suitable for measuring the density of powdered particles which are small enough to pass through a mesh sieve of 0.63 µm (Flint and Flint, 2002). The measurements and parameters obtained from the procedure are presented in Table 5.5. The particle density is also used with the sample bulk density to obtain the total porosity in the sample (Table 5.4).

Table 5.5 Density measurements on powdered clay by the pycnometer method.

Item measured	Symbol/ representation	Recorded values
pycnometer wt. (g)	m1	32.3832
pycnometer + rock sample wt. (g)	m2	35.3605
Rock sample wt. (g)	m2- m1	2.9773
pycnometer + solvent wt. (g)	m4	81.6795
solvent wt. (g)	m4 - m1	49.2963
pycnometer + rock + solvent wt. (g)	m3	82.6662
solvent (post-displacement) wt. (g)	m3- m2	47.3057
displaced solvent wt. (g)	(m4 - m1)- (m3- m2)	1.9906
pycnometer vol. (ml)	solvent volume	49.4256
solvent density (g/ml)	ρw	0.9974
Particle density (g/ml)	ρs	1.4912

The method uses a pycnometer Type 3 (Gay-Lussac), 50 mL volume flask, with close-fitting stopper. The testing 'solvent' is water; all measurements were taken at room temperature. (25^{o}C) and recorded to the nearest 0.0001 g on an analytical scale. Particle density (ρs) = ($\rho w(m2-m1)$)/((m4-m1)-(m3-m2)).

The curves in Figure 5.2 show the relationship between measured densities of the pore size distributions, as well as the cumulative porosities, and their corresponding pore radii. Cumulative porosity at every pressure increment is derived from the volume of 'intruding' mercury (intrusion volume), sample volume and computed total porosity. The cumulative porosity increases gradually with negligible change in the pore radius until it reaches about 0.08 where a significant increase in the pore diameter did not have corresponding effect on it (Figure 5.2 'b'). The curve 'a' shows how density distribution is affected by varying pore sizes. The distribution increases steadily over a wide range of decreasing pore radius, but starts to fluctuate as the pore radius nears its lowest possible limit for the measuring instrument.

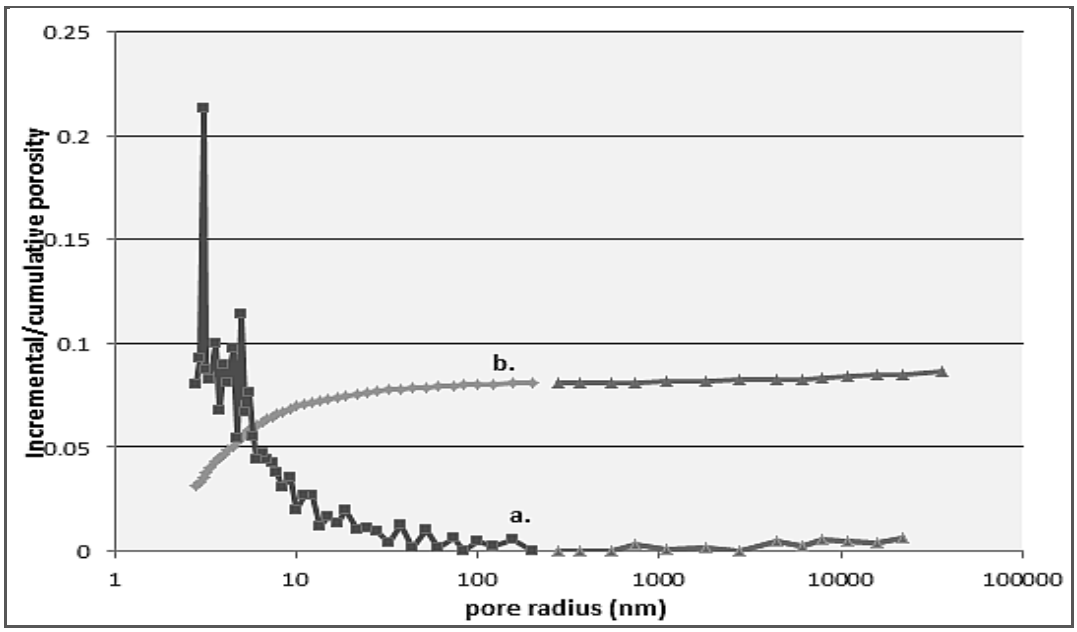


Figure 5.2 Relationship curves of: a) Density distribution vs. pore radii and; b) Cumulative porosities vs. pore radii; the pore radii are measured at increasing pore pressures.

5.2.2. *Geochemical Data*

Geochemical characterization of the Kimmeridge Clay and the North Sea oil was carried out to determine their compositions prior to the laboratory migration experiments.

Saturate and Aromatic Hydrocarbons

Full composition analysis results of both samples are presented in Appendix VI-b. In the Kimmeridge rock extracts, saturates are about twice as abundant as the aromatic hydrocarbons (~7000 ppm/3000 ppm). The *n*-alkanes dominate the saturates distributions with carbon numbers in the range C_{10}-$C_{33,}$ an average total yield of about 2800 ppm and highest individual component yield of up to 454 ppm (C_{23}). This is followed by the terpanes at approximately 1900 ppm; regular steranes at a little over 1000 ppm and then the diasteranes with considerably lower concentration of ~100 ppm. C_{30}-αβ-hopanes constitute barely 10% of the terpane concentration in the rock extract. Pristane and phytane total just over 1000 ppm and are, each, higher in concentration than the largest *n*-alkane. The *n*-alkane and homohopane distributions for both samples are shown in Figure 5.3.

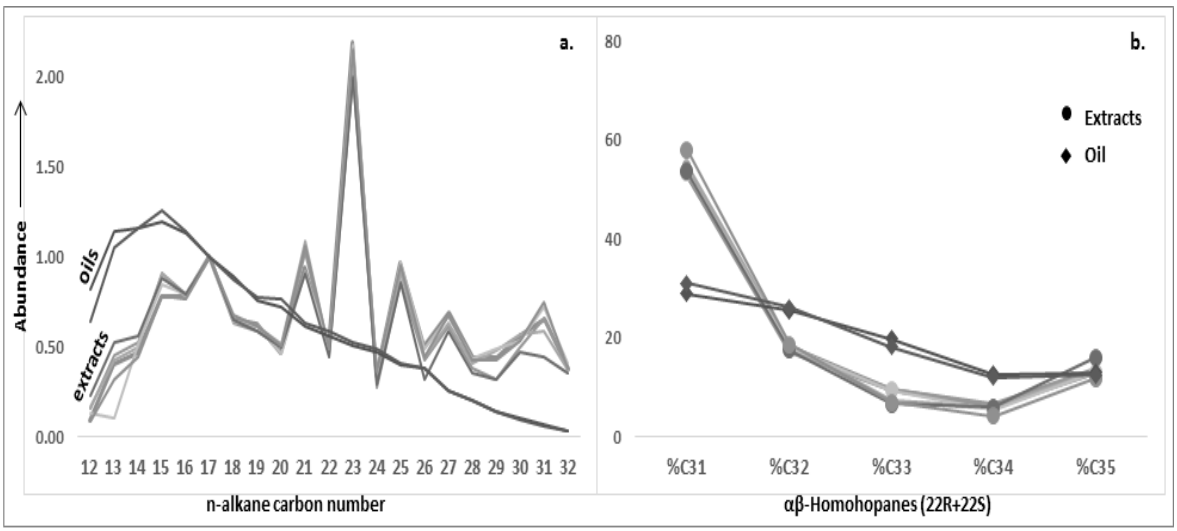


Figure 5.3 Plots showing (a) the distribution of C_{12}-C_{32} *n*-alkanes, and (b) distribution of 22*R*+22*S* C_{31}-C_{35} 17α(H),21β(H)-homohopanes in the replicated Kimmeridge Clay extracts (2x-3●) and North Sea oil (2x-♦). *n*-alkane abundance is normalised to C_{17} *n*-alkane; the homohopane distributions are expressed as a % of total C_{31}-C_{35} hopanes.

Similarly, the aromatic fraction accounted for up to 3000 ppm of the extract with alkylated naphthalenes dominating the distribution (>2000 ppm), followed by phenanthrenes and dibenzothiophenes (DBTs), both with almost equal summed concentrations of about 250-300 ppm. Triaromatic steroids (~45 ppm), biphenyls (~30 ppm), fluorenes and other relatively low abundance aromatic compounds constituted the rest of the EOM's aromatic fraction. Figure 5.4 consists of partial mass chromatograms showing the distribution of significant compounds in the aromatic fractions of both samples.

The North Sea oil summed concentrations of identified saturated compounds from replicate analyses was up to 80000 ppm, which was much more abundant than the aromatic hydrocarbons (>10000 ppm). The *n*-alkanes (~73000 ppm) dominated the saturated fraction with more than 85%; followed by the isoprenoid alkanes (Pr + Ph ≥5500 ppm), the triterpanes (~1200 ppm), the diasteranes (>850 ppm), and then the steranes with about 800 ppm. The aromatic fraction of the North Sea oil constituted major compounds similar to those identified in the rock bitumen and they include the alkylated naphthalenes with the highest summed concentration of up to 6000 ppm (>50% of the aromatic fraction), phenanthrenes with 2700 ppm, and DBTs with a significantly lower abundance of ~800 ppm.

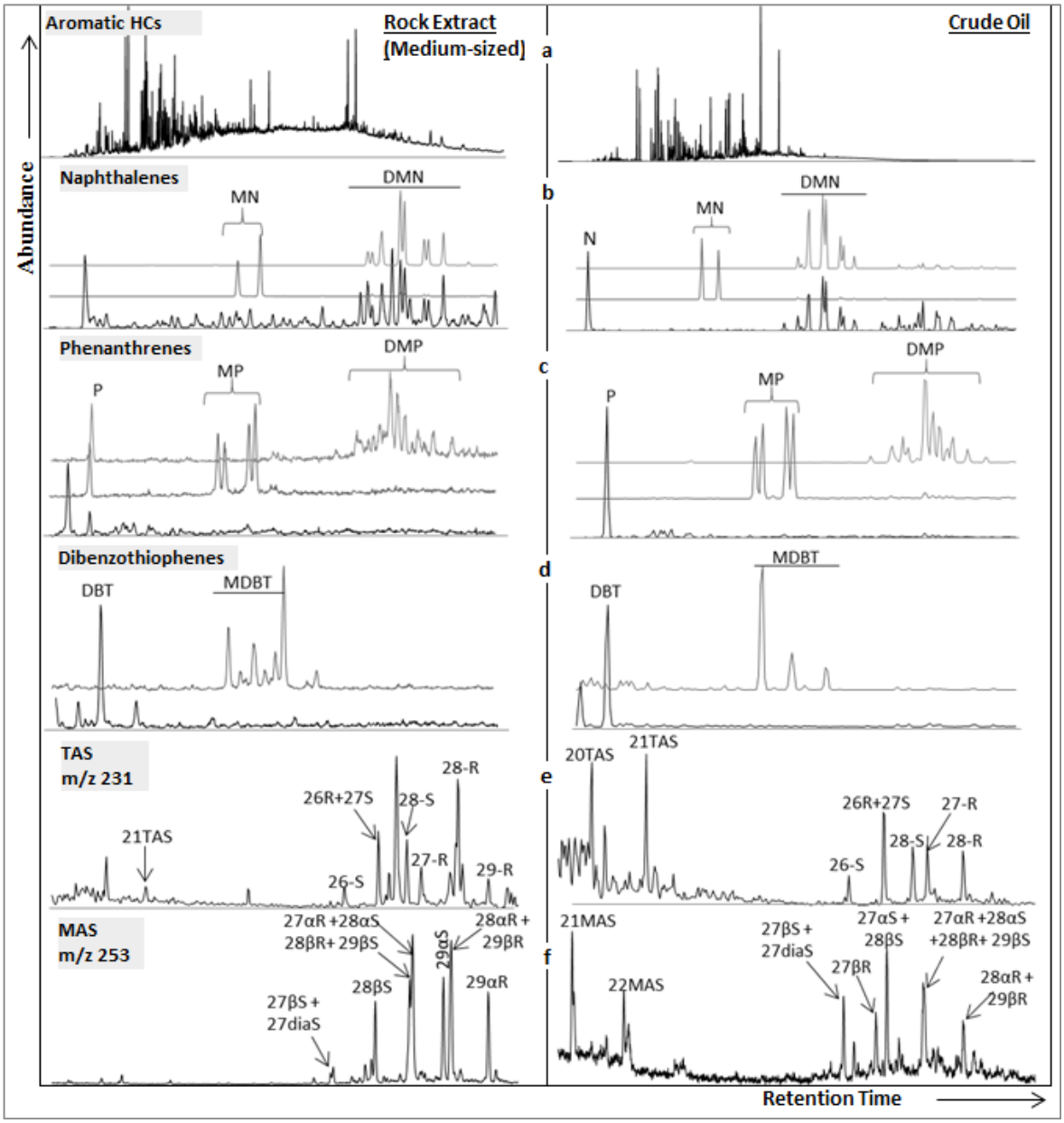


Figure 5.4 GC-MS traces showing the distributions of aromatic hydrocarbons in the Kimmeridge Clay (medium-sized particles) extract and North Sea oil: a) Total ion chromatogram (TIC) of whole aromatic fraction; b) Distributions of naphthalene (N, m/z 128), methylnaphthalenes (MN, m/z 142,) and dimethylnaphthalenes (DMN, m/z 156); c) m/z 178, 192, 206 mass chromatograms showing the distribution of phenanthrene (P), methylphenanthrenes (MP) and dimethylphenanthrenes (DMP); d) distribution of dibenzothiophene (DBT) and methyldibenzothiophenes (MDBT) from m/z 184 and 198 mass chromatograms; e) Mass chromatogram (m/z 231) showing the triaromatic steroid (TAS) hydrocarbons; f) m/z 253 mass chromatograms showing distribution of the monoaromatic steroid (MAS) hydrocarbons. Full peak identification, where needed, is given in Appendix II.

Molecular Maturity and Source Parameters

Table 5.6 shows selected biomarker ratios and parameters derived from analysis data of Kimmeridge Clay extracts and the North Sea oil (NSA03). All values are shown for the replicate analysis of the oil and extracts of the three particle-sized clay samples. These

parameters were used to characterise the samples in terms of thermal maturity, type and depositional environment of the organic matter.

The chromatograms and distribution curves in Figure 5.5 and Figure 5.3 respectively, show the distribution of the *n*-alkanes in the Kimmeridge Clay (medium-sized particles) extract and North Sea oil; the distributions indicate a marine depositional environment, organic matter input and origin (e.g. Farrimond *et al.*, 1984). The Pr/Ph ratios are typically (<1; 0.73-0.76) indicative of a reducing (anoxic) depositional environment for the Kimmeridge Clay (Peters and Moldowan, 1993). The isoprenoid/*n*-alkane ratios are somewhat similar, in application, to the isoprenoid ratios. They are relatively high (>2) in the Kimmeridge Clay extract, characteristic of low thermal maturity and marine organic matter input (e.g. Peters *et al.*, 2005). On the other hand, the North Sea oil (Pr/Ph ratio ~1.24, Pr/*n*-C17 <0.6) appears as a low wax oil from marine-sediments (e.g. Peters and Moldowan, 1993). Although these ratios are used for inference of redox conditions in mature rocks, care must be taken when using this ratio to make inferences on redox or depositional environment for immature rocks and for ratios in the range, 0.8-2.5 as the application has been shown to be superficial in both scenarios without supporting data (Volkman and Maxwell, 1986). This could be due to the effect of thermal maturation and various, other sources of the isoprenoids in the case of Pr/Ph ratios, and the reducing effect of biodegradation on the *n*-paraffins prior to the isoprenoids (Peters and Moldowan, 1993).

The sterane dominance over the hopanes (sterane/hopane ratios), extended hopane distributions, absence of oleananes, distribution of the C_{27}-C_{29} regular and iso-steranes, sterane isomerisation parameters and other maturity-related biomarkers in the Kimmeridge extract (Table 5.6), agree with earlier assessment of the Kimmeridge Clay sample as an immature sediment of predominantly marine organic matter Type-II kerogen (Figure 5.1), which was deposited in a reducing to anoxic environment. As would be expected for an extract with low maturity, C_{31}-C_{32} 17β(H),21β(H) hopanes were identified in the Kimmeridge Clay extract, with a ββ content of ~25% (Table 5.6). Following a similar approach, the North Sea oil is a mature oil, sourced from a Type II organic matter marine shale which had been deposited in dysoxic-anoxic, open marine environment. The high abundance of gammacerane in the Kimmeridge Clay extract (~0.95 ppm) and its relatively lower concentration in the oil (~0.13 ppm) is a reflection of the a stratified water column in the source rock depositional environment, possibly brought about by high salinity (e.g. Farrimond *et al.*, 1984).

Table 5.6 Selected geochemical and biomarker parameters for the Kimmeridge extract and North Sea oil.

Sample	Rock extracts						North Sea oil				
(Dup. run)	Coarse-1	Coarse-2	Medium-1	Medium-2	Fine-1	Fine-2	NS1	NS2	Ave	SD	RSD %
Pr/Ph	0.75	0.75	0.76	0.76	0.74	0.73	1.23	1.24	1.24	0.01	0.79
Pr/nC17	2.38	2.36	2.34	2.35	2.22	2.23	0.55	0.54	0.54	0.00	0.60
Ph/nC18	4.81	4.92	4.82	4.77	4.63	4.50	0.50	0.50	0.50	0.00	0.55
nC17/nC27	1.45	1.50	1.63	1.70	1.59	1.47	3.89	3.81	3.85	0.05	1.31
CPI-1	0.88	1.00	0.72	0.79	0.98	0.89	0.90	0.91	0.91	0.00	0.07
DiaSt (%)	2.4	3.0	3.5	4.7	1.9	2.3	59.6	57.8	58.7	1.2	2.1
St29S/R	0.20	0.20	0.16	0.20	0.17	0.17	1.28	1.39	1.33	0.08	5.72
St29I/R	0.40	0.45	0.47	0.44	0.51	0.56	1.72	1.47	1.59	0.18	11.18
%27St	34.0	31.8	32.0	32.0	31.9	31.1	43.1	42.4	42.7	0.5	1.1
%29St	47.6	49.5	48.7	48.8	49.2	49.8	25.1	25.6	25.3	0.3	1.3
%St27Iso	28.2	26.6	28.0	27.1	26.9	27.1	38.8	38.7	38.7	0.1	0.2
%St28Iso	31.4	29.9	31.9	28.7	32.6	32.1	32.4	32.0	32.2	0.3	0.8
%St29Iso	40.4	43.5	40.1	44.2	40.5	40.8	28.8	29.3	29.0	0.3	1.2
C29/C27	1.23	1.31	1.30	1.30	1.30	1.34	0.70	0.71	0.71	0.01	1.62
St29/Tt30	4.80	4.79	4.46	8.88	6.48	6.92	12.79	16.74	14.77	2.80	18.95
Ts/Tm	0.35	0.35	0.36	0.37	0.44	0.37	2.94	1.92	2.43	0.72	29.65
Hop/Mor	0.80	1.03	0.66	1.04	0.92	0.94	5.18	5.28	5.23	0.07	1.26
Dia/NorM	0.24	0.24	0.22	0.20	0.22	0.23	6.50	6.66	6.58	0.11	1.66
29Ts/29Tm	0.19	0.22	0.20	0.25	0.27	0.25	0.83	0.81	0.82	0.01	1.77
Hop(35/34)	2.12	2.44	2.08	2.67	2.24	2.77	1.03	1.04	1.03	0.01	1.00
Gam-I	0.95	0.95	0.98	0.92	0.96	0.93	0.14	0.13	0.13	0.01	4.81
HHI	0.56	0.55	0.56	0.54	0.56	0.51	2.10	1.84	1.97	0.19	9.60
%22S (C31)	29.1	28.6	29.3	26.7	28.1	29.5	56.5	56.2	56.4	0.2	0.3
%ββ (C31)	26.2	25.3	24.9	25.3	25.5	25.3	n.d	n.d	n.d	n.d	n.d
MPI(1)	0.50	0.55	0.56	0.57	0.57	0.55	0.65	0.63	0.64	0.02	2.64
MPR	0.61	0.59	0.64	0.65	0.67	0.67	0.92	0.97	0.95	0.03	3.38
DBT/PHEN	1.26	1.60	1.73	1.57	1.13	1.14	0.18	0.17	0.18	0.00	1.29
TAS/MAS	0.00	0.01	0.01	0.02	0.01	0.01	4.70	6.33	5.52	1.15	20.90

Pr/Ph = pristane/phytane; Pr/nC_{17} and Ph/nC_{18} = ratio of pristane, phytane to related *n*-alkanes; 17, 18 and 27 = carbon number of respective *n*-alkanes; CPI-1 = (2*C_{29})/(C_{28}+C_{30}); DiaSt(%) = % C_{27}-13β,17α- (20*S*+*R*) diasteranes in total C_{29} (20*S*+*R*) ααα+αββ steranes and C_{27}-diasteranes; St29*S*/*R* = 20*S*/20*R* ααα-C_{29} steranes; St29I/R = (20*S*+20*R*)-αββ/ααα-C_{29}- Steranes; %C_{27} and %C_{29}St = ααα-20*R*-C_{27} and –C_{29} as % of sum C_{27}-C_{29}-ααα-20*R* sterane; %St27-29Iso (m/z 218) = C_{27}-C_{29} (20*R*+20*S*) iso-steranes as % sum C_{27}-C_{29} αββ steranes; C_{29}/C_{27} = C_{29}/C_{27} ααα-20*R* steranes; St29/Tt30 (Sterane/Hopane) = sum of all m/z 217 C_{29} regular and Iso-steranes/αβ-C_{30}-hopane; Ts/Tm = 18α(H)-22,29,30-Trisnomeohopane (C_{27}Ts)/17α(H)-22,29,30-trisnorhopane (C_{27}Tm); Hop/Mor =αβ-hopane/βα-hopane (moretane); Dia/NorM = C_{30}-17α-Diahopane/βα-30-nor-C_{29}-Moretane; 29Ts/29Tm = 18α-30-norneohopane/C_{29}-αβ-Hopane; Hop(35/34) = ratio of (22*S*+22*R*) αβ-C_{35}-homohopane to αβ-C_{34}-homohopane; Gam-I (gammacerane index) = C_{30}-gammacerane/C30-αβ-hopane; HHI = relative abundance of C_{31}-C_{35} homohopanes (22*S*+22*R*) to C_{27}-C_{30} hopanes; %22S(C_{31}) = % 22S in 22*S*+22*R*-αβ-C_{31}-hopan; %ββ(C_{31}) = C_{31} ββ/(ββ+βα+αβ)22*S*+*R* expressed as a %; MPI-l = 1.5*(2MP+3MP)/(P+IMP+9MP); MPR = 2MP/1MP; MDR-1 = 3+2/1MDBT; DBT/P = dibenzothiophene/phenanthrene; TAS/MAS = relative abundance of C_{26}-C_{28} TAS to C_{27}-C_{29} MAS. The NS 'original' oil is shown as a set of averaged figures with corresponding standard deviation (SD) and relative standard deviation (RSD) values.

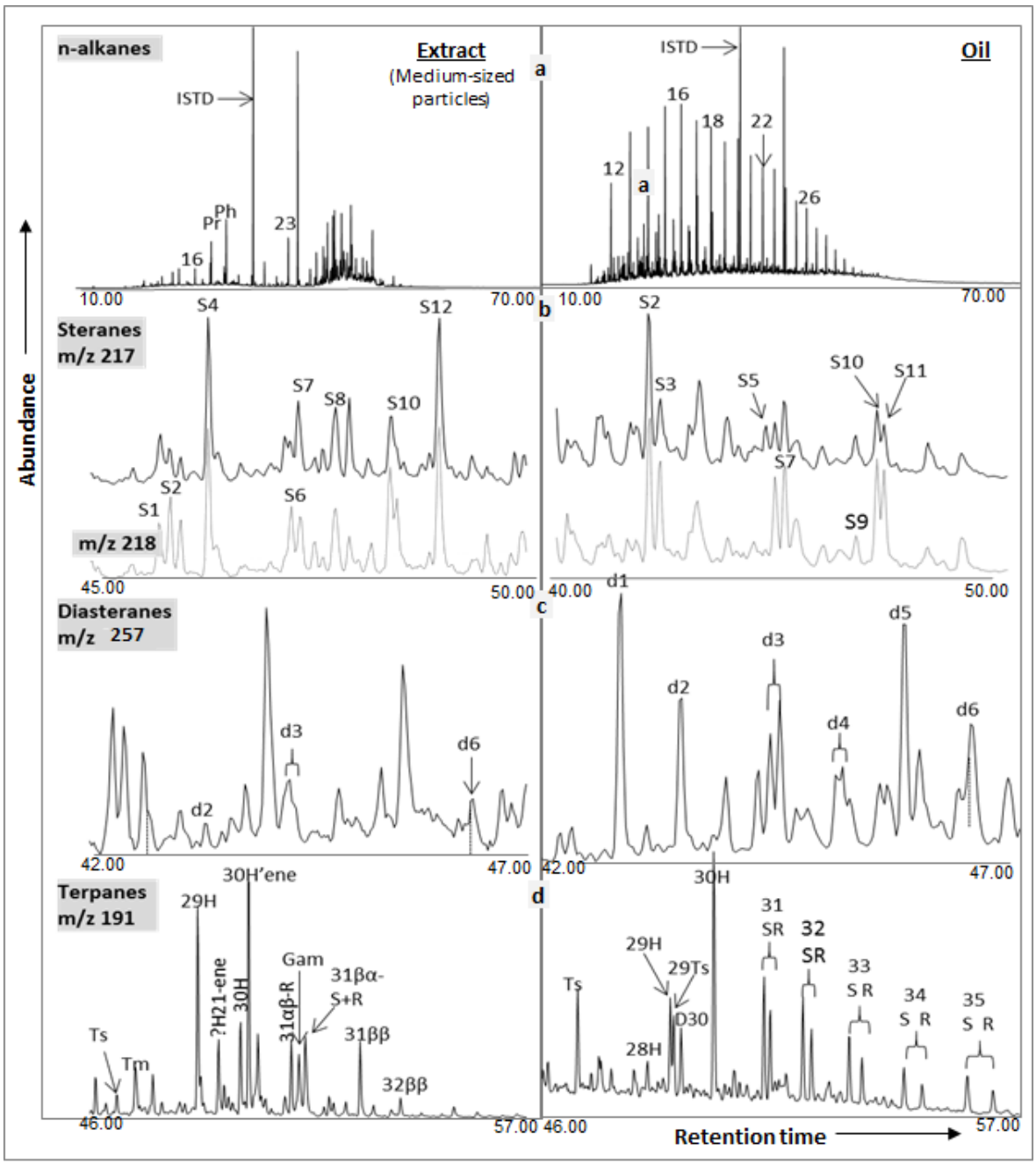


Figure 5.5 Distributions of saturated hydrocarbons detected in the Kimmeridge Clay (medium particle size) extract and a North Sea oil. a) Gas chromatograms of the saturated hydrocarbon fractions show distributions of normal and isoprenoid alkanes; b) Distributions of C_{27}-C_{29} regular steranes from m/z 217 and m/z 218 mass chromatograms; c) mass chromatograms (m/z 257) showing the distributions of diasteranes; d) m/z 191 mass chromatograms showing the distributions of triterpanes. The sterane and diasterane peaks are denoted as 'S' and 'd' respectively. Full peak identifications are given in Appendix II.

The C_{29}/C_{27} sterane ratios in the Kimmeridge extract and the North Sea oil sample showed the dominance of the C_{29}- over the C_{27}- steranes which, though minimal, is an indication of some degree of terrestrial/plant organic matter contribution to the marine sediments (Figure 5.6). The lithologies of the oil source rock and, also for comparison, the Kimmeridge Clay sample, were inferred using a tri-plot of the C_{29}-C_{31} hopanes (Appendix III-d) which groups both samples into marine carbonate clay and marine shale oil families. This was also confirmed by the histogram of relative abundance of diasteranes to the total steranes (DiaSt

(%), Table 5.6, Table 5.7), the dibenzothiophene/phenanthrene ratio, and its relationship with the isoprenoid alkanes ratios (Table 5.7) (Hughes *et al.*, 1995). The high DiaSt (%) of the North Sea oil is an indication of a clay-rich source (e.g. Cornford *et al.*, 1983, Peters *et al.*, 2005).

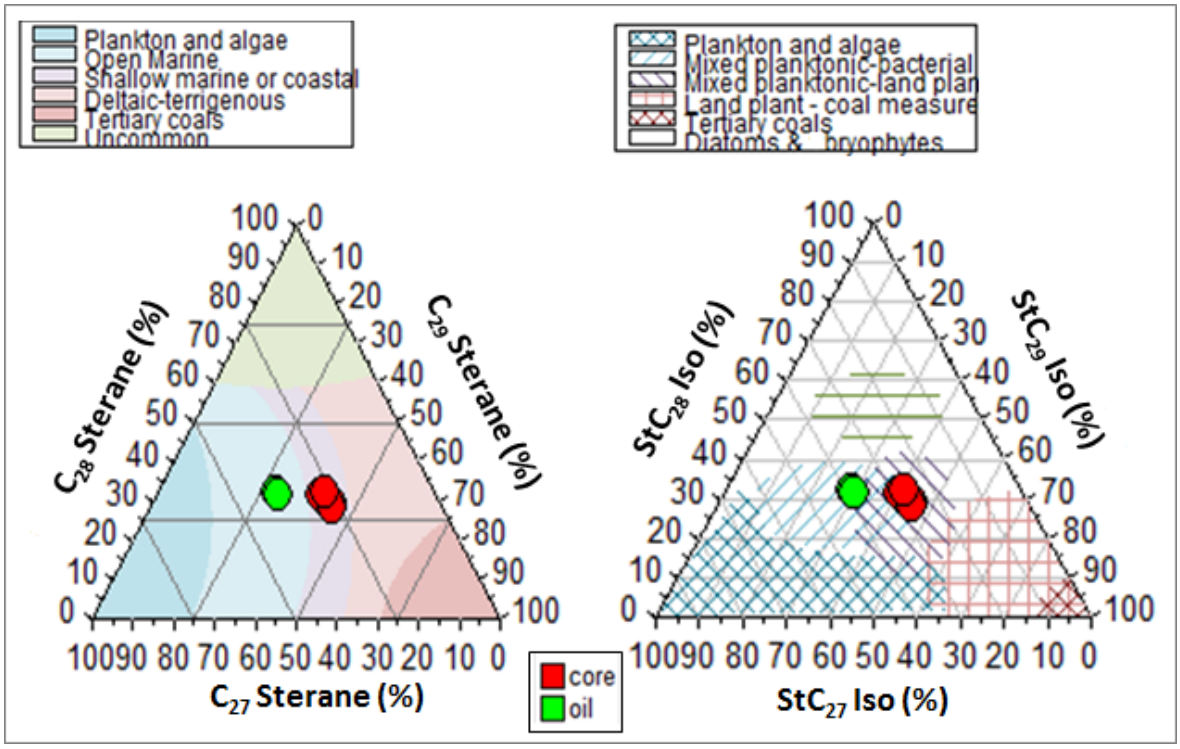


Figure 5.6 Ternary plots showing the relative distribution of ααα-20*R* and αββ- C_{27}–C_{28}–C_{29} steranes in the Kimmeridge extract and North Sea oil for inference of source rock kerogen type and depositional environment. Overlays derived with pIGI software.

The TAS28*S*/*R* ratios (≥ 0.80; Appendix IV-b), abundance of long-chain MAS and TAS relative to total steroidal hydrocarbons and the TAS/MAS ratios (Table 5.6) all indicate the differing thermal maturities in both samples as well as indicating the mineralogy of the oil source rock (Peters and Moldowan, 1993). A summary of the geochemical characteristics that define the Kimmeridge Clay extract and the North Sea oil are presented in Table 5.7.

Table 5.7 Summary of the main characteristics of the Kimmeridge Clay extracts and the North Sea oil prior to the migration experiment.

Characteristics	Determinant (ratios, parameters, plots)	Rock (KCF) extract	North Sea oil	Example References
Thermal maturity	Pr/nC_{17} vs. Ph/nC_{18}; St29S/R; St29I/R; DiaHop/NorM vs. Hop/Mor; ββ-hopanes; C_{27}- and C_{29}-Ts/Tm; %Diast/St; TAS/MAS; T_{max}	Immature	Highly mature	Radke (1988); Farrimond *et al.* (1984); Espitalie *et al.* (1985); Peters and Moldowan (1993)
Anoxia	Pr/Ph; Pr/nC_{17} vs. Ph/nC_{18}; histogram of extended (C_{35}/C_{34}) hopanes	Reducing- Anoxic	Dysoxic–Anoxic	Farrimond *et al.* (1994); Peters and Moldowan (1993); Sonibare *et al.* (2008);
Kerogen Type	Sterane/terpane ratios; C_{29}/C_{27}-Steranes; C_{27}-C_{29} iso-sterane ternary plot; S_2 vs. TOC	Type-II; mixed planktonic-land plant	Type-II; mixed planktonic-bacterial	Peters *et al.* (2005); Snowdon (1991); Espitalie *et al.* (1985)
Organic matter	Sterane/terpane ratios; Pr/nC_{17} vs. Ph/nC_{18}	Marine	Mixed (marine + terrestrial)	van Aarssen *et al.* (2000); Philp (1994); Curiale *et al.* (2005)
Depositional Environment	$\%C_{27}$-C_{29} regular sterane ternary plot; gammacerane index;	Hypersaline, shallow/coastal marine	Saline, open marine	ten Haven *et al.* (1985); Pang *et al.* (2003); Peters and Moldowan (1993); Marynowski *et al.* (2007)
Source rock Lithology	Diasteranes (% DiaSt); DBT/Phen (clay = >1, oil = <1); DBT/Phen vs. Pr/Ph (Appendix III-d); C_{29}-C_{31} hopane tri-plot; Hop/Mor	Carbonate (sulphate-rich)	Shale (clastic?)	Peters *et al.* (2005); Hughes *et al.* (1995); Pang *et al.* (2003)
Migration/ Alteration	Pr/Ph vs. nC_{17}/nC_{27}, n-alkane GC fingerprint; Pr/nC_{17} vs. Ph/nC_{18}; St29S/R vs. St29I/R; $\%C_{31\text{-}35}$ HHI	Low-mature, slightly biodegraded	'Normal' (non-fractionated), mature	Farrimond *et al.* (1984); Peters and Moldowan (1991); Curiale and Bromley (1996b)

The determinants include biomarker ratios and parameters as well as the relationship plots and diagrams from which each characteristic inference has been drawn. Ratios, parameters and diagrams which are not referenced in Table 5.6 or in the main thesis body are referred to in designated Appendices (e.g. Appendix III-d).

Olefin and Acid Contents of the Kimmeridge Clay and the North Sea oil

The solvent extracts of the three particle-sized fractions of the Kimmeridge Clay (4 mm-1 mm; 1 mm-63 µm; <63 µm), and the North Sea oil samples were analysed for olefinic hydrocarbons and carboxylic acids and the results summarised in Table 5.8.

Normal olefins (*n*-alkenes) were not detected in any of the extract samples, but relatively very low amounts (TnA ~16 ppm) were measured in the oil. As would be expected, however, oleanenes were absent in both samples. This is in contrast to the observation made of this class of olefins in most of the case study oils discussed in the previous chapter. Sterenes

were also not observed in these samples. The immature Kimmeridge Clay showed total olefin and acid contents of up to 4000 ppm and 6000 ppm, respectively, but the contribution of the hopanoic acids (HA), which are absent in the oil, to the total acid concentration is relatively low (≤ 320 ppm; Table 5.8).

Table 5.8 Abundance of unsaturated hydrocarbons and carboxylic acids in the migration study with the Kimmeridge Clay and a North Sea oil (NSA03).

Olefins (ng/g)				
Sample	Rock extract			NS-oil
	Coarse	Medium	Fine	(NSA03)
Hop-17(21)enes				
30	49827	44059	54264	3
31S	2617	n.d	1779	17
31R	12452	10623	12553	7
32S	578	n.d	341	15
32R	3747	3484	3890	11
33S	n.d	n.d	n.d	11
33R	2945	2750	3241	8
34S	548	464	556	8
34R	1882	2017	2111	5
35S	n.d	n.d	n.d	8
35R	2207	2121	2638	4
Sum Hopenes	76802	65518	81372	98
Diacholest-13(17)-enes				
C27βS	54177	53406	57235	99
27αS	203545	214624	211071	466
C27βR	55314	56030	59314	60
C27αR	245721	254545	251507	391
C28αS	149725	162904	188349	444
C28αR	103654	97299	138088	172
C29αS	482465	473743	557532	852
C29βR	120402	135374	153425	85
C29αR	373346	347162	386969	437
Sum Diasterenes	1788350	1795087	2003489	3006
4β-Me-10α-diasterenes				
C28S	348149	353689	394131	77
C28R	404874	414573	451020	71
C29S	119535	119358	134572	103
C30S+29R	298905	257070	291675	119
?C30x	78627	53159	64045	36
C30R	498821	430741	481104	73
?C30y	167469	142081	155649	42
Sum Me-dia	1916381	1770671	1972196	521
Tot. Olefins	**3781533**	**3631276**	**4057057**	**3625**

Carboxylic Acids (µg/g)				
Sample	Rock extract			NS-oil
	Coarse	Medium	Fine	(NSA03)
Linear acids				
nC12	147	161	320	n.d
nC13	156	147	323	n.d
nC14	182	102	245	n.d
nC15	156	99	259	3
nC16	270	106	555	8
nC17	189	141	386	1
nC18	212	104	327	6
nC19	123	71	171	n.d
nC20	123	60	338	n.d
nC21	106	87	378	n.d
nC22	150	42	188	n.d
nC23	89	22	229	n.d
nC24	178	75	305	n.d
nC25	59	67	104	n.d
nC26	59	51	125	n.d
nC27	46	32	240	n.d
nC28	59	75	238	n.d
nC29	51	69	201	n.d
nC30	53	74	274	n.d
nC31	38	13	31	n.d
nC32	38	69	235	n.d
nC33	31	19	89	n.d
nC34	52	1	100	n.d
Pr-acid	48	155	400	1.0
Ph-acid	60	76	187	1.4
TnA (Corr.)	2647	1766	6157	16
Hopanoic acids (HA)				
C30	2	0	0	n.d
C31	32	12	7	n.d
C32	228	61	48	n.d
C33	65	13	12	n.d
Sum HA	327	86	66	n.d
TA (nA+HA)	2973	1852	6224	n.m

Total olefins = sum C_{30}-neohopene + C_{31}-C_{35}- hop-17(21)enes + sum of all diaster-17,21-enes + sum methyl-diasterenes (4β-Me-10α-diasterenes); linear acids include the normal and isoprenoid (pristanic and phytanic) acids; TnA (Corr.) is the corrected total acid which, by calculation, eliminates the amount of acids contributed by possible contamination; nC_{12}-C_{34} are approx. values with no consideration for possible contaminants; C_{30}-C_{33} hopanoic acids sums identified isomers (αβ, βα and ββ) of each carbon series; Sum HA = C_{30}+C_{31}+C_{32}+C_{33} hopanoic acids; TA (total acid) = TnA + SumHA. Both groups of compounds were measured in ppb/ppm (ng/g or µg/g) depending on the amount of component present; n.d means component was not detectable; n.m means non-measurable data due to very low concentration or absence of the compounds.

The C_{32}-HA homologues are prevalent in all three Kimmeridge Clay particle size variants. In the crude oil, the sum concentration of identified olefins is very low, while observed linear acids occur in negligible quantities. Compared with those of the rock extract, as shown in

Figure 5.7, the HA in the North Sea oil is below detection limit or absent. This Jurassic Type-II-sourced North Sea oil is regarded as a mature oil which had probably not travelled through any immature organic-rich rocks during its migration and accumulation (cf. Jaffé and Gallardo, 1993). Furthermore, the type of organic matter and depositional environments of the sources of these samples are defined by relatively very low amounts of hopenes (~100 ng/g; Table 5.8) compared to diasterenes, whose sum concentration is about 50 times more in the clay and 35 times more in the oil (Table 5.8). This observation compares to those made with the predominance of steranes over hopanes in these samples (Table 5.6) as indication of marine depositional environment of their source organic matter (Peters *et al.*, 2005). It also follows that the high abundance of diasterenes in the EOM of the Kimmeridge Clay is evidence of thermally immature clastic marine-type sediments.

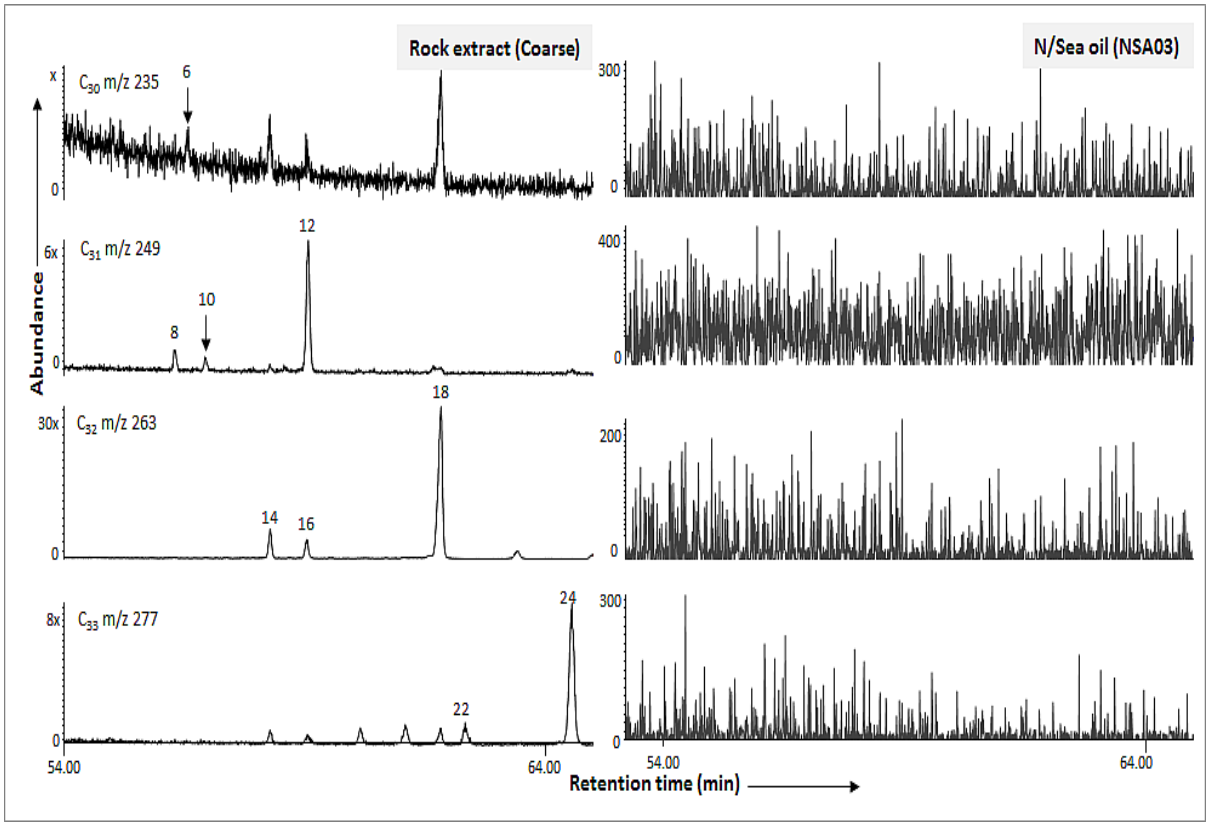
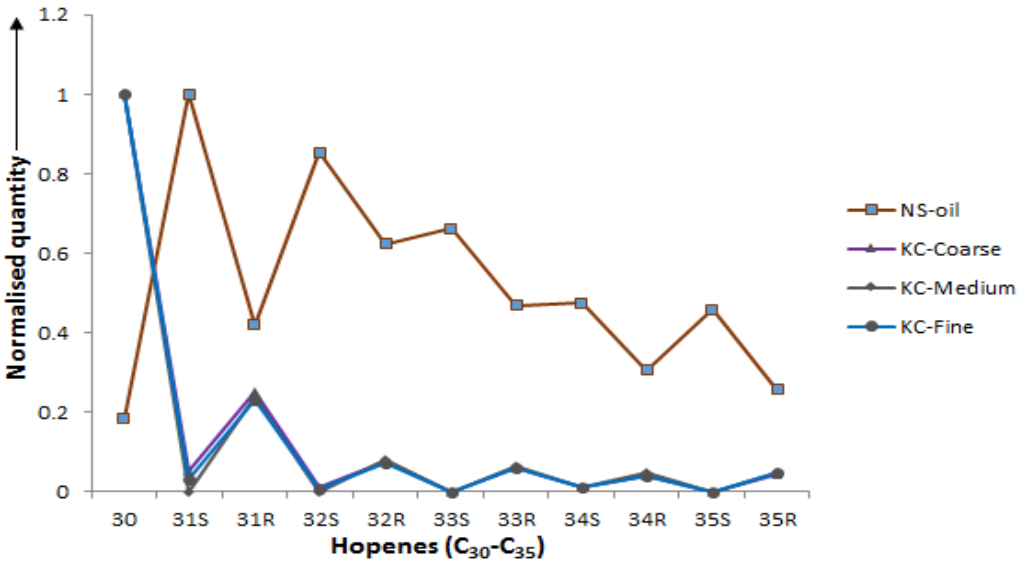


Figure 5.7 Comparison of the hopanoic acid (as fatty acid methyl esters) content in representative Kimmeridge Clay (coarse) extract and the North Sea oil (NSA03) using partial mass chromatograms m/z 235-277 for C_{30}-C_{33} HA homologues. The prominent peaks, 12, 18 and 24 are the ββ-22*R* isomers of the C_{31}-C_{33} HA. The y-axis (abundance) scale of the oil chromatogram is negligible (≤400) compared to those of the extract (up to 30x); x = 1000 units. Full peak identification of the HA isomers is given in Appendix II-f.

There are some large variations in the concentrations of these olefins and acids across the three size fraction extracts of the same clay sample (Table 5.8). Some differences were also observed, but to a lesser extent in the saturated and aromatic hydrocarbon components. It is probable that differences in clay particle size properties (e.g. porosity, surface areas) and the

polarities of the analytes play an important role in recovery efficiencies of these compounds during the analysis processes.

The distribution of the stereoisomers of hop-17(21)-enes clearly seems to be affected by the maturity of the sample pair as demonstrated in the distribution line plot of C_{30} neohopenes and C_{31}-C_{35}-(22*S* and 22*R*) homohopenes in the clay extract and crude oil (Figure 5.8). There are no known published literature on the occurrence of olefins in North Sea oils or similar Jurassic-type oils to compare with or back up the present findings, but evidence of their geochemical characteristics (e.g. Table 5.6 and Table 5.7) correspond with this remarkable contents and their distribution in the said oils. The trends displayed by the two samples (Figure 5.8) are reversed with respect to relative abundance of the homologues and ratios of the two stereoisomers (22*S*/22*R*). The high *S*/*R* ratio in the oil is reversed in the clay extract; and while C_{30} hopene is the dominant component in the immature extract, the homohopenes are more abundant in the oil (also Figure 5.9). This study suggests that this relationship could be influenced by specific depositional environment or organic matter type, but more importantly, by the maturity of the sample source rocks. The North Sea oil (NSA03) used in this experiment has been shown to be mature and non-biodegraded (e.g. Figure 4.20), while consistent evidence of low maturity of the Kimmerigde source rock has been indicated (e.g. Figure 5.5), and consistent with its very high total olefin content (>3500 ppm).



Sample	Hop30	Hop31		Hop32		Hop33		Hop34		Hop35	
		S	R	S	R	S	R	S	R	S	R
NS-oil	0.18	1.00	0.42	0.85	0.62	0.66	0.47	0.47	0.31	0.46	0.26
KC-Coarse	1.00	0.05	0.25	0.01	0.08	0.00	0.06	0.01	0.04	0.00	0.04
KC-Medium	1.00	0.00	0.24	0.00	0.08	0.00	0.06	0.01	0.05	0.00	0.05
KC-Fine	1.00	0.03	0.23	0.01	0.07	0.00	0.06	0.01	0.04	0.00	0.05

22S/R quantities normalised to the highest isomer peak.

Figure 5.8. Distribution of C_{30}-C_{35} hopene (22*S*/22*R*) isomers in the Kimmeridge Clay extracts and North Sea oil. The concentrations (shown in accompanying data) are normalised to the biggest isomer (C_{30} and C_{31} hopenes for the extract and oil, respectively) across samples. Note the reversed distribution of the 22*S* and *R* in both distributions. Component identification is presented in Appendix II-c.

Furthermore, the redistribution of the extended hopenes homologues and their 22*S* and 22*R* isomers in migrated samples is illustrated in the m/z 367 chromatograms shown in Figure 5.9. It could be seen that the extract is dominated by more abundant R isomers while the reverse is the case in the North Sea oil. This unique distribution was significantly altered as seen in the chromatograms for the migrated oil and column extract. The 'column extract' fraction, and what it stands for, have been clarified previously (3.7.1). Here the *S* and *R* isomers are almost equally distributed, an indication that the process is a partial and restricted one. While hopene concentration, though still relatively low, is seen to have increased in the migrated portion, differences in distribution between the *S* and *R* isomers seem to have narrowed (i.e. decreased *S/R* ratios) probably due to solubilisation of more *R* isomers by the migrating oil from the rock particles. This suggests that migration-derived hopenes in altered oils are more sensitive to redistribution than concentration.

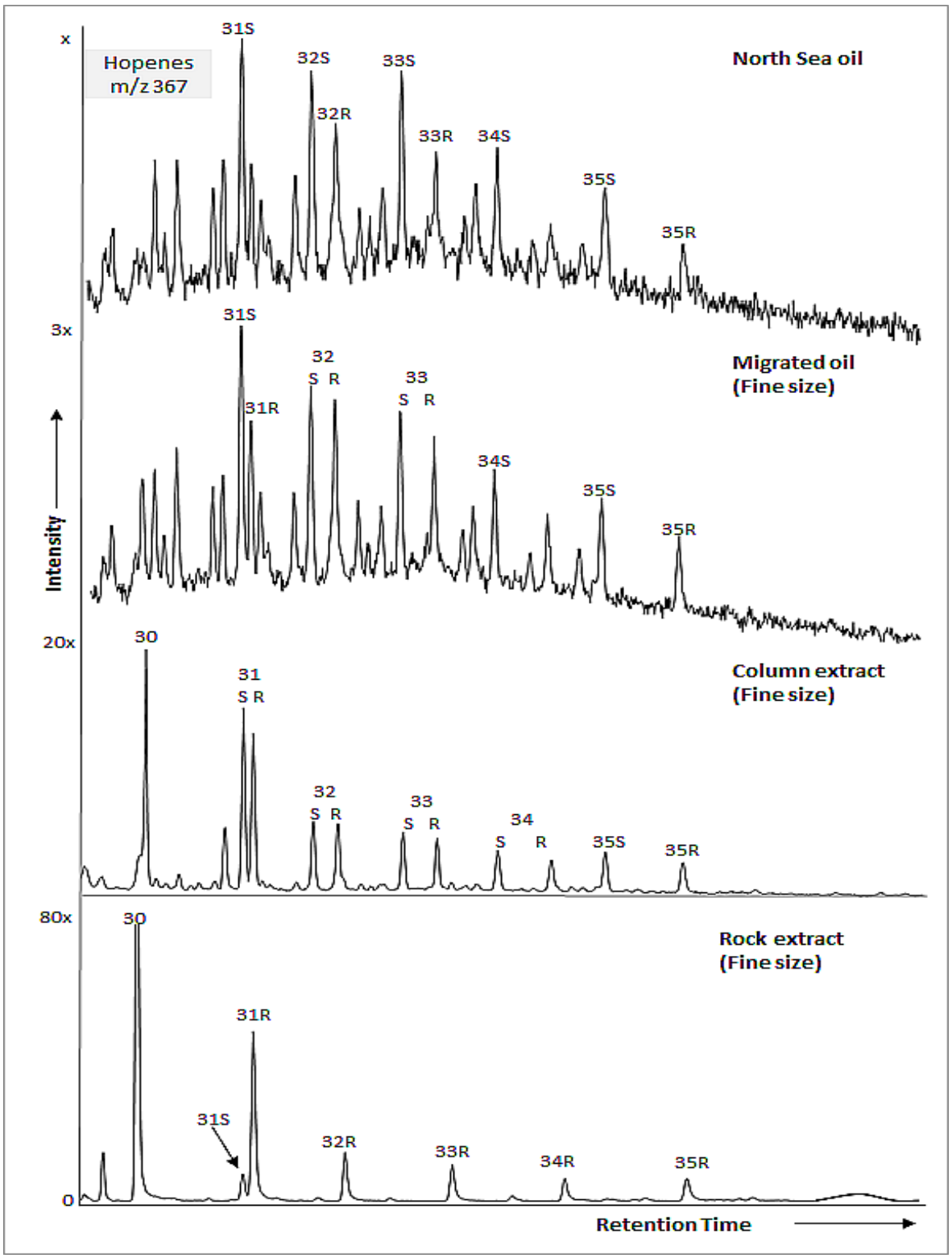


Figure 5.9 m/z 367 chromatograms showing changes in the distribution of the extended hopene isomers (22*S*, 22*R*) in the original oil, its migrated portion (through fine particles), and rock (fine particles) extract, compared with that of the column (fine) extract portion. The intensity scale depicts the relative abundances of hopenes in all three samples;' x' is approximately 100 units. Full peak identification is shown in Appendix II-c.

Figure 5.10 shows the distribution of the hopanoic acids and *n*-acids in the the rock extract variants. The peaks labelled 31-33ββ-*R* are the most prominent 17β(H),21β(H)-22*R* of the isomers in the series across the three extract variants. The C_{30}-C_{33} hopanoic acid distribution

in a rock extract may consist of the three isomers 17α,2lβ, 17β,21α and 17β,21β, whose concentrations and distributions depend on their generation and maturation (Jaffé and Gardinali, 1990). The most themodynamically stable of these are the βα isomers, which increase alongside their αβ counterpart as the thermodynamically least stable ββ-isomers decrease, with increasing maturation (Jaffé *et al.*, 1988b). In the Kimmeridge Clay acid fraction, the distribution is clearly dominated by the isomers with the ββ and 22*R* configuration. In general the C_{32} HA are most prevalent, while the concentrations of C_{30} hopanoic acids concentration are very low to absent (Figure 5.10; Table 5.8). As shown previously (Figure 5.7), the liquid phase, North Sea oil did not contain detectable HA.

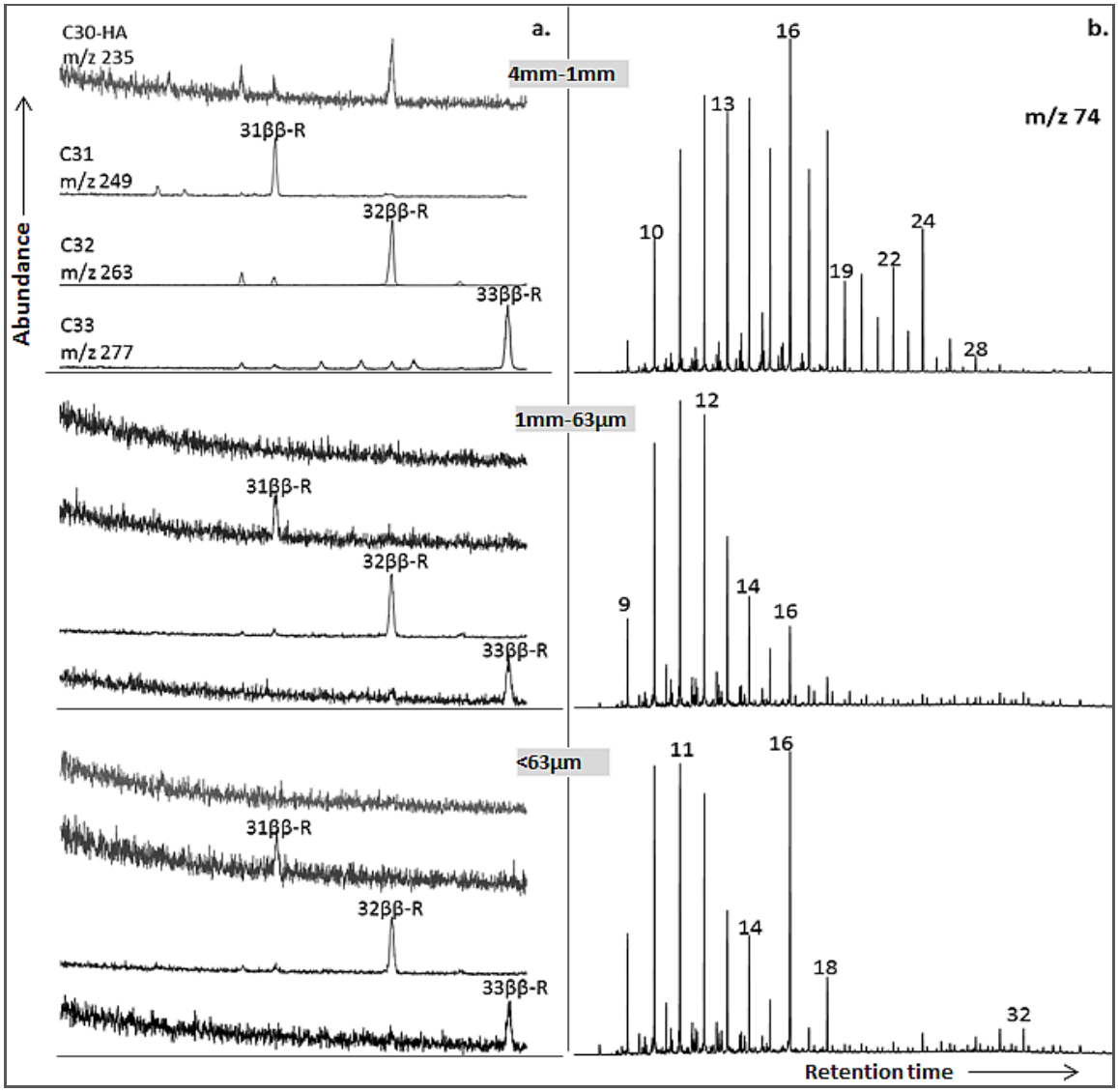


Figure 5.10 Distribution of: a.) hopanoic acids and, b.) *n*-acids (as methyl esters) in the Kimmeridge Clay extract; shown by mass chromatograms m/z 235-277 for the C_{30}-C_{33} HA homologues, and m/z 74 for C_{10}-C_{34} *n*-acids. The integers represent the carbon number or chain length of the corresponding compound peak. Full peak identification of the HA isomers is given in Appendix II-f.

5.2.3. *Simulated Oil Migration*

The experimental set-up for the oil migration simulations was described in detail in Chapter 3. Briefly three particle size variants of the same rock sample were packed individually in HPLC columns through which known volumes of crude oil samples were pumped at controlled flow rates. Aliquots of 'migrated' oils were collected from the end of the column (outlet) at approximate hourly intervals. These oil samples were analysed for the similar classes sought in the original samples prior to the migration experiment. The following observations, with respect to the olefins and acids quantities and redistribution, are based on the present set-up, and correspond to recorded flow, volume and interval scales of migrated oils as summarised in Table 5.9.

Olefins & Carboxylic Acids: Concentration Differences and Redistribution

The olefinic hydrocarbons detected in the migrated crude oils are generally classed into the same groups detected in the Kimmeridge Clay extracts. They include the hop-17(21)enes, diaster-13,17-enes and the methyl-diasterenes (4β-Me-10α-diasterenes). No normal alkenes or oleanenes were detected. The distribution profiles of identified olefins and carboxylic acids in the 3 rock extract variants were compared with those of 'migrated' oils for possible changes in the concentration and distribution of these compounds. The solid phase rock particles, through which the oil migrates in this simulation experiment, had high olefin content relative to the North Sea oil (Table 5.8). Where a 'simple' migration-contamination mechanism is in place, enrichment of the North Sea oils by incorporation of olefins and fatty acids contained within the matrix of rock particles through which the oil migrates, was expected. Figure 5.11 shows how the concentration of olefins (hopenes, diasterenes and methyl-diasterenes) have generally changed (increased) over an approximately six-hour time scale. Although these changes are gradual and unsteady across the eluents, consistent patterns, from the 'coarse' to 'fine' migrated oil portions, can be observed clearly (Figure 5.11, concentration data table in Appendix IV-a). Olefin profiles in the 'fine' variant of the migrated eluates are remarkably different from those of the 'coarse' and 'medium' variants. This pattern is shared by all three olefin groups in the oils eluting through fine-sized particles.

Only the relatively short-chain *n*-acids (C_{12}-C_{18}- SCA), maximizing at either C_{16} or $C_{18,}$ were detected in the migrated oils, as opposed to the presence of both short and long-chain acids in the rock extracts, which were in considerably higher concentrations (concentration data

in Appendix IV-a). Hopanoic acids were absent in all collected eluents, however, significant amounts of these acids were detected in the 'column' extract (content of the steel column briefly extracted by covering with enough dichloromethane (DCM) and standing for about 3 minutes).

Table 5.9 Summary of main measurements observed and recorded at various stages in the migration study.

A. Migration experiment measurements

Rep 1	Column Wt (g)	Column Vol. (ml)	Rock bulk density (g/ml)	Start flow (ml/min)
	309.7	19.64	1.359	0.5

Particle sizes-→	Coarse	Medium	Fine
Col+spent rock wt (g)	331	331	330.1
Spent sample wt (g)	17.9	n.m	9.4
Col.extract Wt. (g)	2.4	3.7	3.4
Col.ext density (g/ml)	n.m	0.8222	n.m
saturation time (min)	n.m	16	35
Column dead vol. (ml)	9.0	9.4	n.m
Sample vol (ml)	10.7	10.2	n.m
Packed sample wt (g)	14.5	13.9	8.1

Rep 2	Column Wt (g)	Column Vol. (ml)	Rock bulk density (g/ml)	Start flow (ml/min)
	309.8	19.64	1.359	0.5

Particle sizes-→	Coarse	Medium	Fine
Col+spent rock wt (g)	332.5	333.8	329.8
Spent sample wt (g)	21.0	21.5	19.5
Col.extract Wt. (g)	5.7	5.2	9.6
Col.ext density (g/ml)	0.8507	0.8387	0.8348
saturation time (min)	17	16	29
Column dead vol. (ml)	9.0	8.0	14.0
Sample vol (ml)	10.7	11.6	5.6
Packed sample wt (g)	14.5	15.8	7.6

B. Migration flow, volume and time scales corresponding to results of analysed migrated samples

Rep 1	Coarse			Medium			Fine		
Mig oils	Flow rate1 ml/min	Interval hr	Oil Vol. ml	Flow rate2 ml/min	Interval hr	Oil Vol. ml	Flow rate3 ml/min	Interval hr	Oil Vol. ml
a1	0.1	2	5.4	0.1	1	6.5	0.1	1	5.6
b1	0.1	2	5.0	0.1	1	6.0	0.1	1	6.0
c1	0.15	2	6.5	0.1	1	6.0	0.1	1	5.8
d1	0.2	1	4.8	0.1	1	6.0	0.1	1	5.9
e1	0.2	1	4.8	0.1	15	90.0	0.1	1	5.9
f1	0.2	17	83.0	0.1	1.11	6.8	0.1	1	5.9
g1	0.2	1	4.9	0.1	1	5.9	0.08	18	59.9
col1	0	0	n.a	n/a	0	4.5	n/a	n/a	n.m

Reps 2	Coarse			Medium		Fine	
Mig. oils	Flow rate ml/min	Interval hr	Oil Vol. ml	Interval hr	Oil Vol. ml	Interval hr	Oil Vol. ml
a2	0.1	1	6.0	1	6.6	1	5.6
b2	0.1	1	6.0	1	6.0	1	5.8
c2	0.1	1.13	6.8	1	6.0	1	6.0
d2	0.1	0.87	5.2	1	6.0	1	5.9
e2	0.1	1	6.0	1.03	6.2	1	6.0
f2	0.1	1	6.0	1	6.0	1	5.9
g2	0.05	16	48.0	16.5	50.0	16	48.0
col2	0	0	6.7	0	6.2	0	11.5

Weights, volumes and time intervals were correspondingly measured and recorded for the columns (HPLC), rock particles and oil samples prior to, and at key stages of the migration experiment. The bottom table (B) shows the quantities (flow rate, volume of oil and travel time) corresponding to migration-contamination observed in the migrated samples in two replicate runs (Rep 1 and Rep 2). Greyed rows show eluted oils collected over a 15-18 hour (overnight) period.

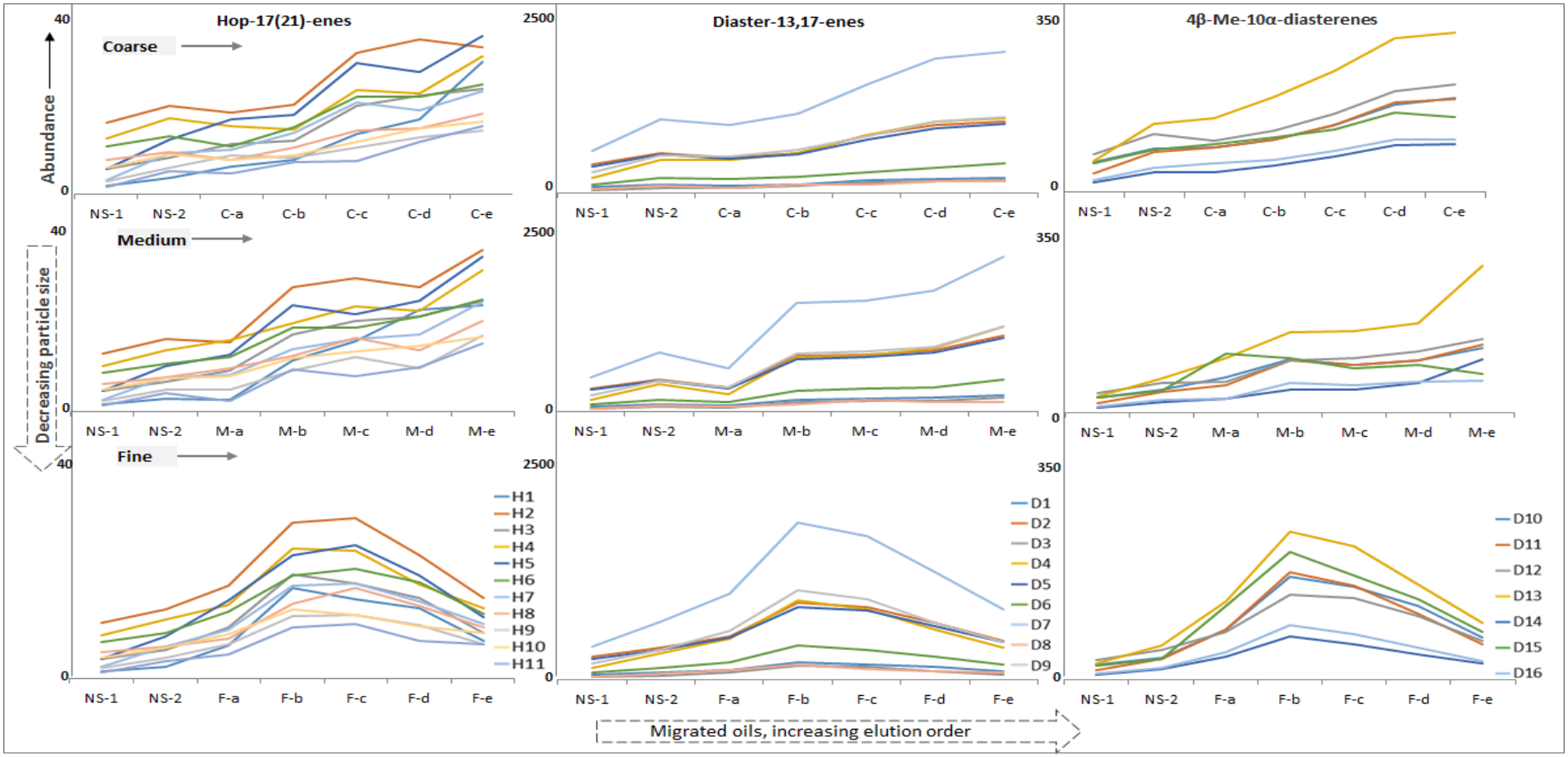


Figure 5.11 Line plots showing the abundance profiles of identified olefins in the migrated oils from the first migration run, in order of elution and collection at 1-2-hour intervals. These show a clear change in the concentrations of the olefins in the oil following its travel through the clay-packed HPLC column. The profiles are seen to be similar across the three size variants especially in the migrated oils from the fine-sized particles. The x-axes denoted NS1-2, C-a-e; M-a-e, and F-a-e are the oil duplicate, coarse, medium and fine-sized migrated oils variants respectively; portions 'a' = first eluent and 'e' is the last eluent in corresponding particle size migration variants. The abundance units are measured in ng/g and show the relative abundances of the olefins in the oils. Oil volumes and the migration time scales corresponding to these observations are shown in Table 5.9. Key to plot line identification is shown in Table 5.11.

The acid profiles of the 'migrated' oils are represented in Figure 5.12. Although no clear distribution trends are apparent, it is worthy to note that both normal and hopanoic acids were, respectively, very low (~16 µg/g) and below detection limits (<0.25 µg/g) in the initial oil prior to the migration experiment. The concentration of *n*-acids in the 'migrated' oil fractions may have been enriched due to migration-contamination from the rock components. It is not clear why the hopanoic acids were not solubilised by the migrating oil but this could possibly be due to differences in adsorption (geochromatographic effect) and, hence, the retention of the acids by the rock matrix (cf. Jaffé and Gallardo, 1993). This effect is evident in observed significant amounts of hopanoic acids in the column extracts, post-migration as shown in Table 5.10. Sufficient contact time between the oil components and those of the solid mineral phase may be necessary for effective acid solubilisation; time element is very negligible in a laboratory experiment relative to what is obtainable in an actual field scenario, and this could also represent a significant factor. Furthermore, the actual porosity and permeability of the source rock may also have been altered by the crushing of the rock and column packing of the particles prior to the simulation. Jaffé *et al.* (1988a), and Jaffé and Gallardo (1993) thought that these rock properties determine the efficiency of acid incorporation during the migration process.

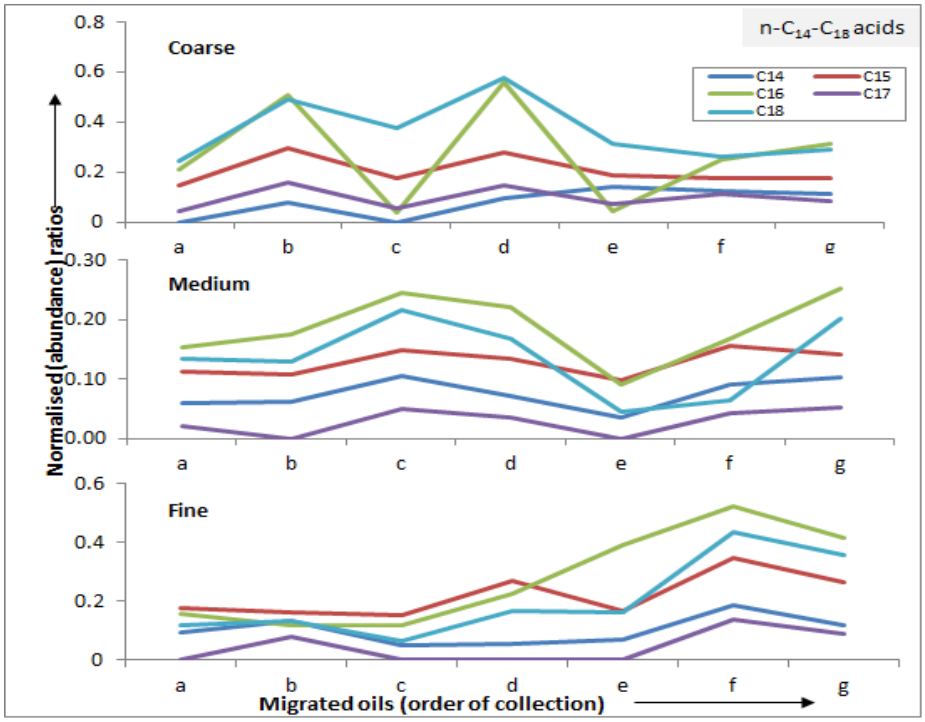


Figure 5.12 Acid profiles in 21 'migrated' oils showing distribution ratios of C_{14}-C_{18} *n*-acids. Changes are seen to be generally unsteady across the three migrated oil variants but an increasing trend is noticeable in the fine-sized eluates. Negligible amounts of acids were observed in the initial oil. The y-axis units are normalised ratios of the *n*-acid abundances in the migrated oil to those measured in corresponding column extracts. The x-axis labels are the migrated oils in the order in which they were collected: a, b, c…, and g; 'a' being the first eluate and 'g' the last collected portion; respective oil variants are designated as Coarse, Medium and Fine accordingly.

Table 5.10 Data comparison of acid abundance in the rock and column extracts.

		Concentration (ppm)						
Sample type	Mesh size	30-HA	31-HA	32-HA	33-HA	HA	TnA	TA
Column extract	Coarse	0.26	0.36	1.94	0.54	3.10	83	86
	Medium	0.30	1.12	7.47	2.39	11.28	190	201
	Fine	0.24	0.79	3.83	1.12	5.99	93	99
Rock extract	Coarse	1.73	32	228	65	327	2647	2973
	Medium	n.d	12	61	13	86	1766	1852
	Fine	n.d	7	48	12	66	6157	6224

Both samples each consist of three particle size variants (coarse, medium and fine).TnA is a factor corrected total *n*-acid content which eliminates the amount of acids contributed by possible contamination; 30-, 31-, 32-, and 33-HA are sum concentration of identified isomers (αβ, βα and ββ) within corresponding C_{30}-C_{33} hopanoic acid homologue; HA = C_{30}+C_{31}+C_{32}+C_{33} hopanoic acids; TA (total acid) = TnA + HA. 'n.d' means component was absent or not detectable.

Routine Hydrocarbon Biomarker Compounds

Many of the routine biomarker compounds, particularly the aliphatic hydrocarbons, had high concentrations in the initial crude oil (Figure 5.5; Figure 5.4; Table 5.6). Under the present simulation conditions, the alteration effect of migration-contamination on the aliphatic and aromatic hydrocarbon composition of the original oil was not noticeable when computed data and selected ion traces were visually compared. For instance, the overlaid terpane fingerprints of the rock extract, original North Sea oil and the possibly 'contaminated' migrated oil (a middle eluate) in Figure 5.13, were compared for possible signs of compositional changes and redistribution. The 'migrated' oil looked much the same as the original crude oil. This was also suggested by the computed quantities of the terpenoid compounds (Appendix III-b) which do not differ significantly, at first glance, in the three samples.

In addition, the m/z 191 mass chromatogram of aliphatic hydrocarbon fraction of the rock extract also revealed high relative abundance of a prominent peak (suspected as hop-17,21-ene), which eluted just before the βα-C_{29} hopane peak; and another C_{30}-hopene peak, eluting just after the αβ-C_{30}-hopane (30H) in the rock extract. Neither olefin peaks were observed in the 'fresh' nor 'migrated' oil mass ion traces (Figure 5.13). The detection of an expected change in distribution of these compounds could have been hindered by the massive differences in the scale of unsaturated hydrocarbons vs. saturates (in this instance) found in the Kimmeridge sample compared to those in the North Sea oil. It would be difficult to notice low concentration compounds like the olefins, in this example, within highly abundant aliphatic compounds just by looking at the chromatograms alone. Migration effects were

assessed for individual class of compounds in order to minimise the limitations of these differences between individual measuring scales.

Saturates: This study had also attempted to evaluate previous works, as well as validate present findings on the incidence of migration-contamination of oils by indigenous olefins and acids, which suggested that the redistribution of saturate hydrocarbons may become disturbed during migration through sources rocks of certain lithologies (e.g. Bonilla and Engel, 1988, Brothers *et al.*, 1991).

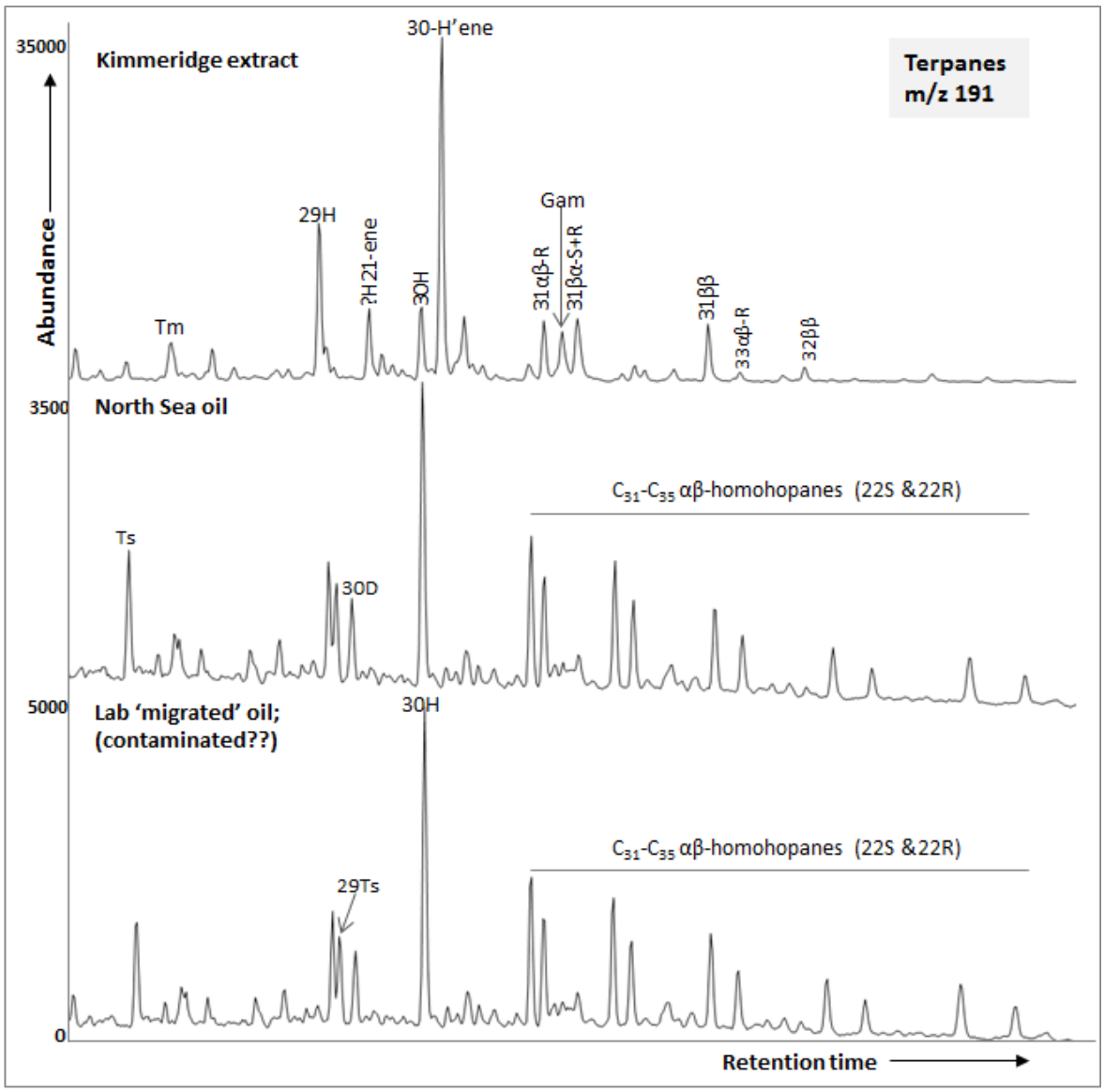


Figure 5.13 Selected m/z 191 mass chromatograms showing triterpenoid distributions in the saturate fraction of the Kimmeridge Clay extract and the North Sea oil prior to migration and subsequent representative 'migrated' oil. No visible redistribution is observed in the 'migrated' oil to suggest the occurrence of migration-contamination owed to the terpenes in the rock extract. Full peak identity is given in Appendices II-b and II-c.

In order to determine whether the present simulated migration of oil through a Kimmeridge Clay Blackstone revealed detectable changes in the distribution of *n*-alkanes, terpanes and steranes, line plots of concentration data of selected homologues of these compounds in the

saturate fractions of the migrated North sea oils were generated. Distributions were shown and compared for oil from the three clay particle variants: coarse, medium and fine (4 mm-1 mm; 1 mm-63 μm and <63 μm). The *n*-alkanes profiles (Figure 5.14A) revealed redistributions of lower molecular weight components (C_{12}-C_{20}) over their higher molecular weight counterparts (C_{22}-C_{32}), with increasing elution intervals. The higher homologues could be seen to show no detectable change in their distribution throughout the migration run by their almost flat profiles within the distribution. In addition no accentuation of the *n*-alkane distribution was appreciably favoured by a particular size of clay packing during migration. In all three attempts (x2 replicate runs) at passing the North Sea oils through the crushed clay mud rock, only slight changes in the *n*-alkane abundances were recorded (Appendix IV-a). These findings uphold other previous results of similar investigations (e.g. Bonilla and Engel, 1988).

The migrated oils were also slightly enriched in terpanes and steranes as suggested by chromatographic data (Appendix IV-b) and displayed line plots in Figure 5.14B. The αββ-20*R* sterane isomers dominated the sterane distribution in the original oil; this dominance was, however, unaltered in the 'migrated' oils as could be seen from the distribution (Figure 5.14B) and concentration data (Appendix III). Only the C_{27}-αββ-20*R* sterane was seen to show some cumulative concentration increase in the 'migrated' oils. Also shown in Figure 5.14B, the diasteranes exhibited much the same distribution behaviour as the sterane; and they appeared to be unaffected by conditions of the present migration system. Similarly, the profiles of the terpane series were also observed (Figure 5.14B). Many of the terpane compounds revealed some degree of changes in their concentrations over the migration period while some others were unaltered. Again, the αβ-C_{30}-hopane seems to have been most affected by the migration effects among this saturate group as indicated by its distinct increasing trend on the terpane plot (Figure 5.14B). In general, the above findings reinforced the fact that, although some saturate compounds may have undergone some compositional or distributional changes during migration, these effects are usually small compared to their actual concentrations in the sample(s) being investigated.

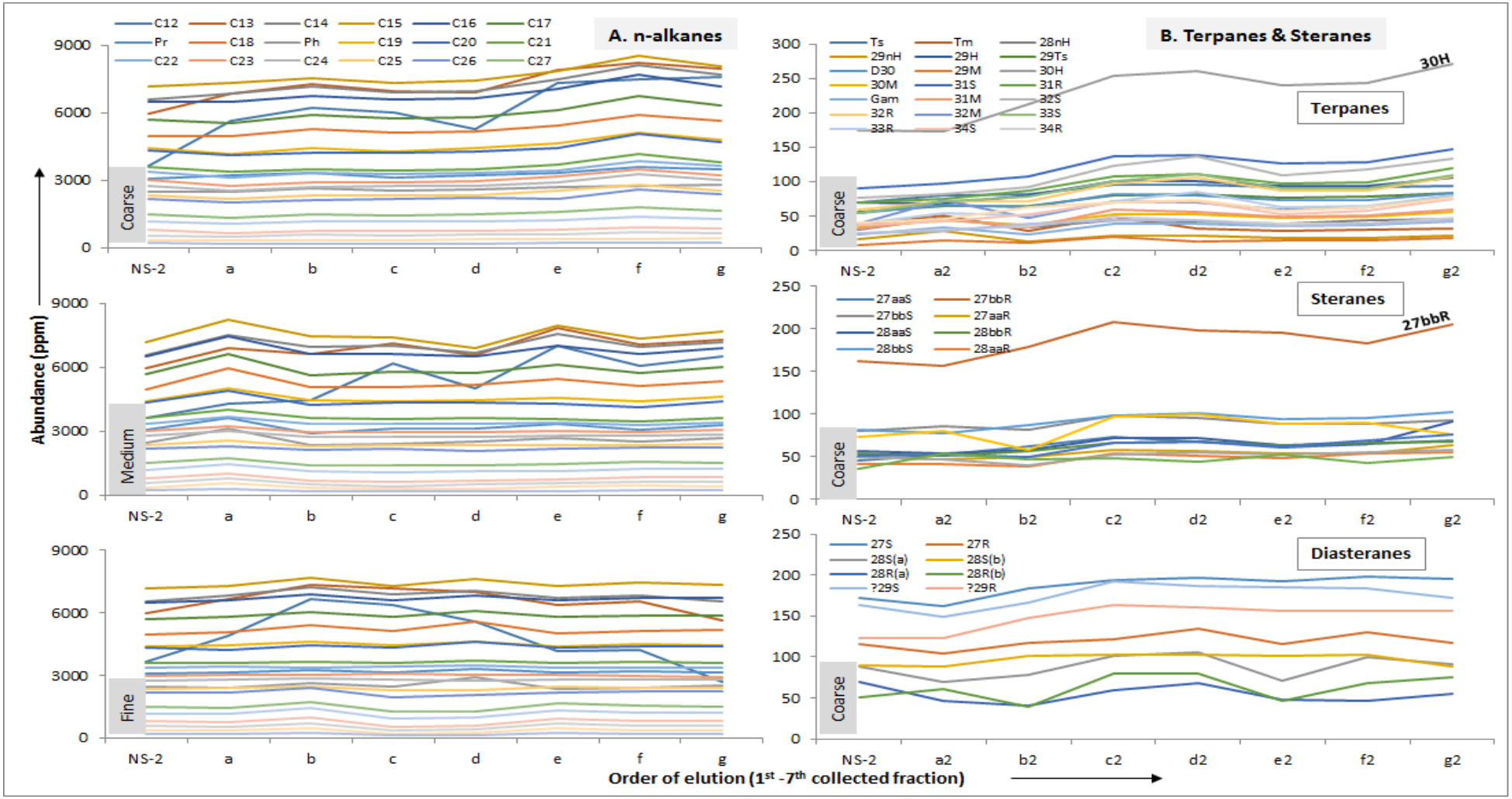


Figure 5.14 Line plots showing the distribution profiles of A) *n*-alkanes and B) pentacyclic terpanes and steranes in the saturate fractions of the North Sea oil with increasing migration order/intervals (portions 'a'→ 'g'). The solid phase packing consisted of Kimmeridge Clay particles of varying sizes (coarse, medium, and fine). The x-axes represent actual migrated oil portions in the order they were collected at ~hourly intervals, having passed through either the coarse, medium or fine-sized particles, in HPLC column outlet. Disturbances to distribution of the *n*-alkanes are observed in lower molecular weight (C_{12}-C_{20}) compound. Full legend identification is shown in Appendices II-a, and II-b.

Aromatics: The aromatic compounds are more individual in their responses to migration phenomena as shown by their distribution profiles (Figure 5.15 and Figure 5.16). The dibenzothiophene and its methyl derivatives (DBTs) revealed remarkable patterns in their redistributions in aromatic fractions of the oils that migrated through solid phase rock of different particle sizes (Figure 5.15). There seem to be significant differences in the redistribution of these aromatic sulphur compounds in the crude oil (DBTs) during its migration through the different-sized solid phase particles. While eluates of the 'coarse' and 'fine' particles showed concentration profiles that were more scattered along the trends with little or no enrichment of the DBTs within the 'migrated' oils, the 'medium' eluates revealed a smoother trends with seemingly minor enrichment in the oils. The differences between these three variants of the Kimmeridge Clay are mainly particle sizes, their distributions (porosities, pore sizes), surface areas and permeability (due to manual packing). These variations occur on different scale in the laboratory setup from the natural setting. Further study is required, and suggested in a later chapter, for effective reconciliation of these and other factors.

This is significant to verifying the reproducibility of the redistribution effect within duplicate runs on the same solid phase and the consistency of trends from one solid phase variant (particle size) to another. The profiles which were created from the concentration data of duplicate migration runs (Rep1 and Rep2) were very similar (Figure 5.15). However, obtaining precise or uniform reproducibility with manually packed HPLC columns was difficult in many of the migration runs. Major aromatic fraction components including the naphthalenes, phenanthrenes and the TAS compounds also showed varying distribution trends (Figure 5.16). Selected profiles revealed a slight positive change in the concentration of phenanthrene but relatively little alteration for the alkyl-phenanthrenes components (Figure 5.16a); and highly scattered distribution for the naphthalene and their alkyl derivatives (Figure 5.16c) with no clear trend in their abundances. On the other hand, the TAS, biphenyl, fluorene and other aromatic compounds profiles suggested an increasing trend in their quantities (Figure 5.16d).

The implication of these differences especially between runs on the same solid phases could be related to the impact of differing packing conditions (Table 5.9) as seen among some of these runs. These conditions combine the effects of the weight of solid phase in relation to the volume it occupied in the column and the migration flow rate on compound

redistribution. These factors cause variations in bed volumes and possible higher flow rate which explains these differences.

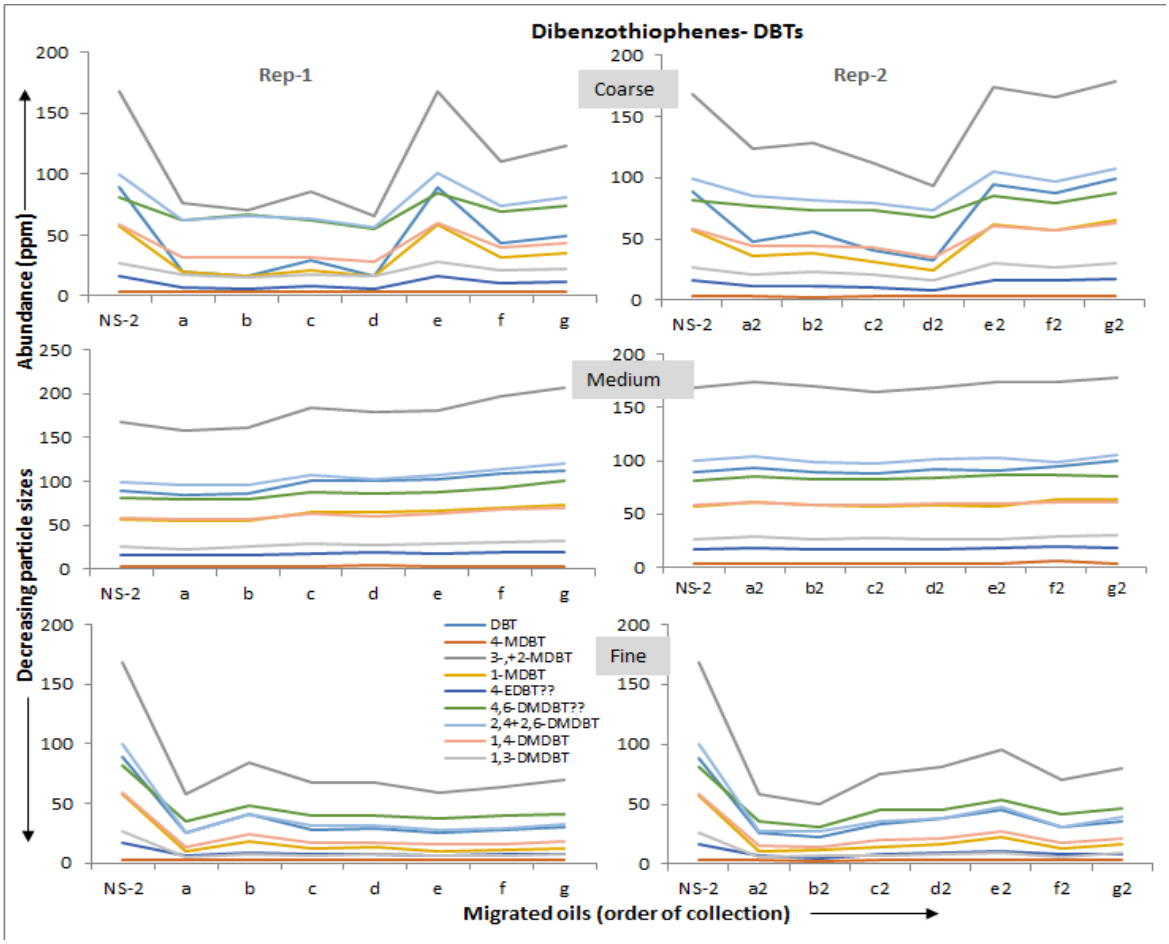


Figure 5.15 Line plots showing the distribution profiles of dibenzothiophene and its alkyl derivatives in the aromatic hydrocarbon fractions of migrated oils in order of elution/collection. The solid phase packing consisted of varying rock particles sizes (coarse, medium and fine) as indicated. The x-axes represent migrated oils via the rock variants, collected at intervals (~hourly) from the outlet. Plots show distinct and consistent DBTs redistribution behaviours in all 3 migrated oil variants; reproducibility is obvious in the replicate run. Full identity of components (legend) is given in Appendix II-g.

It is believed that the high abundances of common aliphatic fraction components relative to the low concentrations of the rare organic compounds is an important factor in the effective assessment of migration-contamination process in crude oil (e.g. Jaffé and Gallardo, 1993). These concentration differences and their effects were also thought to be the reason for the obvious migration-induced changes in the molecular distribution of free carboxylic acids which are present in these oils at very low concentration, unlike the aliphatic hydrocarbons (Jaffé *et al.*, 1988b, Jaffé and Gallardo, 1993). In spite of the above deduction, the likelihood of some degree of variability in these relative abundances in eluted oils was tested further in this work. Owing to the number of measured marker compounds and parameters derived from them, a multivariate statistical technique for analysing this data was used to help achieve the aim of detecting compositional changes in the samples after migration.

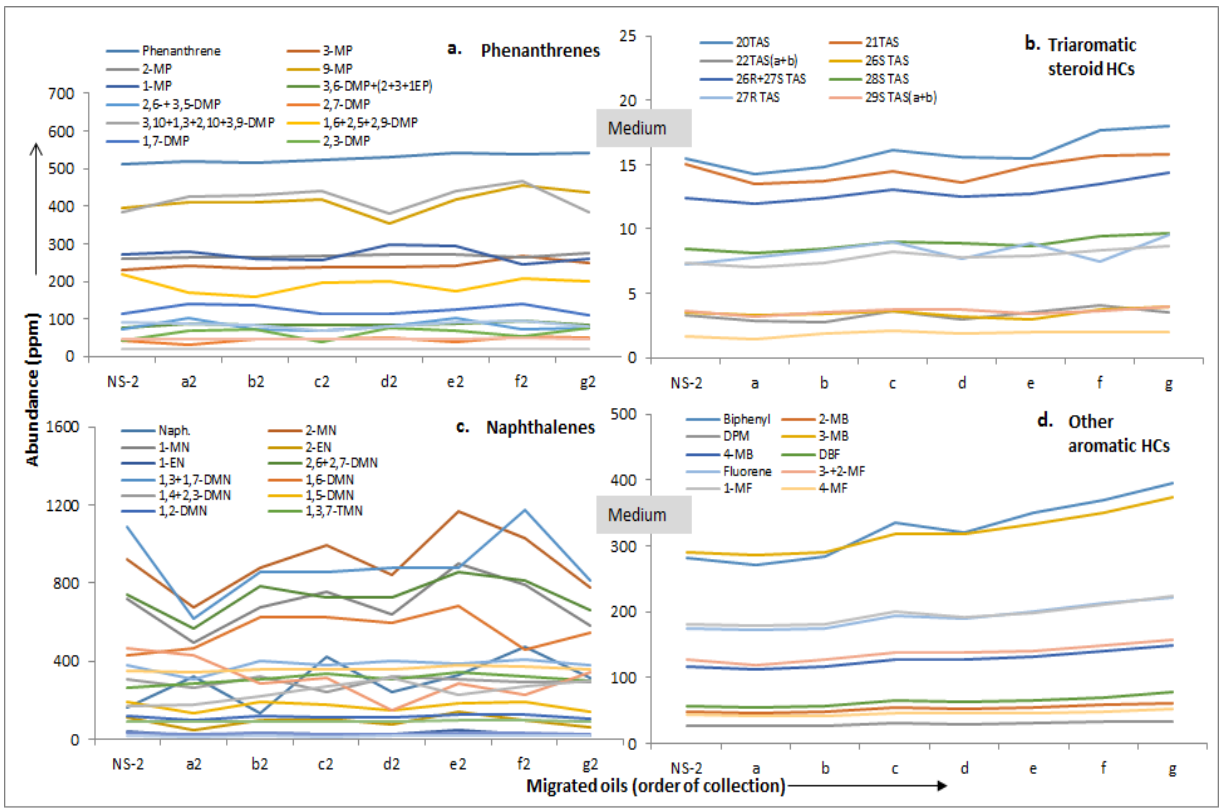


Figure 5.16 Plots of distribution profiles of a) phenanthrene and its alkyl derivatives; b) TAS hydrocarbons; c) Naphthalene and its alkyl derivatives; and d) other aromatic compounds (e.g. biphenyl + alkyl derivatives and fluorene + alkyl derivatives), in the aromatic fractions of the migrated oil portions through columns of medium-sized (1 mm-63 µm) Kimmeridge Clay particles. The x-axes notations, 'a-g', represent the first eluted/collected oil, in that order, to the last eluted oil, 'g'. Full identification is given in Appendix II-g for aromatic compounds.

5.2.4. *Multivariate Statistical Analysis- Principal Component*

Although the above discussions describe the general biomarker characteristics of the migration sample set, as well as indication of their variabilities in 'migrated' oil portions, it is thought that the utility of the large dimensional biomarker data (Appendix IV), generated from the migration study, were limited. Hence, the geochemical molecular marker data, with specific reference to the olefin and acid data, from the above laboratory migration experiments were further analysed and interpreted using principal component analysis (PCA) statistical method. A brief overview of the technique and the analyses could be seen in Appendix IV-e. The outcomes of the PCA and prior analysis are discussed in the following sections.

Data Set and Data Pretreatment

The whole data set comprising of all samples (objects) and biomarker compounds and parameters (variables) are shown in Appendices IV-a, and IV-b. The olefinic and acidic

marker compounds used in the PCA and the codes used to denote them in generated data and graphs are shown in (Table 5.11). Selected established biomarker ratios were also analysed alongside the olefinic hydrocarbons; these are presented, with the codes by which they are denoted, in Table 5.12.

Table 5.11 Olefinic and acidic marker compounds used in the principal components analysis; the codes are used in the analysis data to represent corresponding compounds.

Unsaturated aliphatic hydrocarbons (olefins)		
Hopenes		
H1	C30	Hop-13(18)-ene
H2	C31	Homohop-17(21)-ene 22S
H3	C31	Homohop-17(21)-ene 22R
H4	C32	Bishomohop-17(21)-ene 22S
H5	C32	Bishomohop-17(21)-ene 22R
H6	C33	Trishomohop-17(21)-ene 22S
H7	C33	Trishomohop-17(21)-ene 22R
H8	C34	Tetrakishomohop-17(21)-ene 22S
H9	C34	Tetrakishomohop-17(21)-ene 22R
H10	C35	Pentakishomohop-17(21)-ene 22S
H11	C35	Pentakishomohop-17(21)-ene 22R
Diasterenes		
D1	C27	(20S)-10β(H)-diacholest-13(17)-ene
D2	C27	(20S)-10α(H)-diacholest-13(17)-ene
D3	C27	(20R)-10β(H)-diacholest-13(17)-ene
D4	C27	(20R)-10α(H)-diacholest-13(17)-ene
D5	C28	(20S)-24-methyl-10α(H)-diacholest-13(I7)-ene
D6	C28	(20R)-24-methyl-10α(H)-diacholest-13(I7)-ene
D7	C29	(20S)-24-ethyl-10α(diacholest-13(17)-ene
D8	C29	(20R)-24-ethyl-10β(diacholest-13(17)-ene
D9	C29	(20R)-24-ethyl-10α(diacholest-13(17)-ene
Methyl-diasterenes		
D10	C28	(20S)-4β-methyl-10α-diaster-13,17-ene
D11	C28	(20R)-4β-methyl-10α-diaster-13,17-ene
D12	C29	(20S)-4β-methyl-10α-C28-diaster-13,17-ene
D13	C29/C30	4β-methyl-10α-(C28R+C29S)-diaster-13,17-ene
D14	C30	? 4β-methyl-10α-C29-diaster-13,17-ene
D15	C30	(20R)-4β-methyl-10α-C29-diaster-13,17-ene
D16	C30	? 4β-methyl-10α-C29-diaster-13,17-ene

Carboxylic acids (Fatty acid methyl esters)		
n-acids		
A1	C12	Dodecanoic acid
A2	C13	Tridecanoic acid
A3	C14	Tetradecanoic acid
A4	C15	Pentadecanoic acid
A5	C16	Hexadecanoic acid
A6	C17	Heptadecanoic acid
A7	C18	Octadecanoic acid
A8	C19	Nonadecanoic acid
A9	C20	Eicosanoic acid
A10	C21	Heneicosanoic acid
A11	C22	Docosanoic acid
A12	C23	Tricosanoic acid
A13	C24	Tetracosanoic acid
A14	C25	Pentacosanoic acid
A15	C26	Hexacosanoic acid
A16	C27	Heptacosanoic acid
A17	C28	Octacosanoic acid
A18	C29	Nonacosanoic acid
A19	C30	Triacontanoic acid
A20	C31	Henatriacontanoic acid
A21	C32	Dotriacontanoic acid
A22	C33	Tritriacontanoic acid
A23	C34	Tetratriacontanoic acid
A24	C19	Pristanic (2,6,10,14-tetramethylpentadecanoic) acid
A25	C20	Phytanic (3,7,11,15-tetramethyl hexadecanoic) acid
Hopanoic acids		
HA1	C30	C30 17α(H),21β(H)-22S+R + βα-22S+R + ββ-22S+R
HA2	C31	C31 17α(H),21β(H)-22S+R + βα-22S+R + ββ-22S+R
HA3	C32	C32 17α(H),21β(H)-22S+R + βα-22S+R + ββ-22S+R
HA4	C33	C33 17α(H),21β(H)-22S+R + βα-22S+R + ββ-22S+R

Table 5.12 Selected biomarker parameters used in the PCA. The ratios and indices were measured using peak areas from appropriate GC traces and mass chromatograms.

Sample	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P18	P19	P20	P21	P22	P23	P24	P25	P26	P27	P28
O1	1.23	0.55	0.50	3.9	0.90	59.6	1.28	1.72	43.1	25.1	38.8	32.4	28.8	0.7	12.8	2.9	5.2	6.5	0.8	56.5	0.14	2.1	1.03	0.65	0.92	0.09	0.18	4.70
O2	1.24	0.54	0.50	3.8	0.91	57.8	1.39	1.47	42.4	25.6	38.7	32.0	29.3	0.7	16.7	1.9	5.3	6.7	0.8	56.2	0.13	1.8	1.04	0.63	0.97	0.10	0.17	6.33
M1a	1.26	0.56	0.50	4.1	0.86	56.9	1.03	1.28	32.7	31.6	40.2	31.4	28.4	1.0	13.9	2.5	5.1	5.6	0.9	56.5	0.14	2.1	1.02	0.63	1.08	0.10	0.03	2.26
M1b	1.23	0.55	0.50	4.0	0.87	54.4	1.14	1.49	34.8	31.5	38.6	31.6	29.9	0.9	14.9	2.0	4.9	4.2	0.8	56.1	0.15	2.1	1.04	0.65	0.93	0.10	0.06	2.14
M1c	1.24	0.55	0.50	4.0	0.88	54.1	0.96	1.36	34.2	35.3	39.0	31.2	29.8	1.0	14.6	2.9	4.8	5.5	0.8	56.2	0.15	2.3	1.09	0.65	0.94	0.10	0.03	1.55
M1d	1.24	0.55	0.50	3.9	0.88	53.6	1.18	1.51	35.9	31.3	38.5	31.5	30.0	0.9	14.8	1.9	4.8	5.5	0.8	56.0	0.15	2.1	1.03	0.63	1.01	0.10	0.17	2.64
M1e	1.23	0.55	0.50	3.9	0.87	53.0	1.26	1.60	35.7	30.0	37.4	29.5	33.1	0.8	14.7	3.0	4.8	4.0	0.8	55.7	0.15	2.3	1.04	0.62	1.04	0.09	0.09	1.87
M2a	1.17	0.55	0.52	3.8	0.91	49.4	1.51	0.84	30.8	35.9	37.4	29.7	32.8	1.2	15.2	2.2	4.8	5.0	0.8	56.1	0.15	2.2	1.02	0.64	0.92	0.08	0.17	1.22
M2b	1.30	0.54	0.48	4.2	0.86	52.6	1.27	1.56	37.3	29.9	36.4	29.8	33.9	0.8	15.8	3.0	5.9	6.3	0.8	55.8	0.11	2.0	1.13	0.66	0.93	0.11	0.19	2.95
M2c	1.24	0.55	0.50	4.2	0.85	55.4	1.11	1.28	36.5	32.1	32.4	33.4	34.2	0.9	13.4	1.9	4.8	5.0	0.8	55.7	0.14	2.1	0.99	0.63	1.02	0.10	0.18	3.58
M2d	1.23	0.54	0.49	3.7	0.89	53.9	1.15	1.50	37.8	30.7	37.6	31.6	30.9	0.8	14.0	2.0	5.1	5.0	0.8	55.9	0.14	2.0	1.14	0.66	1.02	0.11	0.18	4.56
M2e	1.23	0.54	0.49	3.9	0.89	56.0	1.04	1.24	35.6	33.0	38.5	31.3	30.2	0.9	13.5	1.9	4.9	4.1	0.8	56.1	0.15	2.2	1.00	0.64	0.93	0.12	0.18	2.47
M3a	1.30	0.54	0.48	4.0	0.88	55.5	1.55	1.32	38.2	29.0	39.6	31.4	29.0	0.8	16.1	3.0	5.3	5.7	0.8	56.1	0.13	2.0	1.04	0.63	0.96	0.10	0.05	1.88
M3b	1.24	0.54	0.49	3.5	0.93	56.0	0.93	1.51	35.5	33.0	37.5	32.0	30.6	0.9	15.6	2.0	5.2	4.7	0.8	56.5	0.14	2.0	1.01	0.65	0.91	0.09	0.09	1.16
M3c	1.34	0.54	0.47	3.5	0.91	56.1	0.98	1.21	33.9	33.5	38.8	31.9	29.3	1.0	14.3	3.2	5.1	6.2	0.8	55.9	0.14	2.2	1.01	0.63	1.01	0.10	0.05	1.44
M3d	1.33	0.54	0.47	3.8	0.91	54.3	0.97	1.41	35.7	33.2	39.2	32.1	28.7	0.9	15.2	2.1	5.5	5.6	0.8	56.2	0.12	2.0	1.10	0.66	0.91	0.09	0.06	1.37
M3e	1.26	0.54	0.48	3.9	0.88	56.1	1.35	1.63	39.5	28.2	38.7	32.0	29.3	0.7	14.8	2.1	4.9	5.7	0.8	55.8	0.15	2.2	1.04	0.66	0.91	0.10	0.06	3.61
M1f	1.22	0.53	0.48	3.7	0.88	53.2	0.87	1.32	32.8	38.1	37.2	29.9	33.0	1.2	66.8	1.6	3.9	4.5	1.0	56.3	0.19	2.0	1.00	0.59	0.86	0.11	0.09	2.87
M1g	1.24	0.54	0.48	3.7	0.87	60.6	0.84	1.23	36.6	35.1	36.4	29.9	33.8	1.0	41.2	2.9	5.8	5.4	0.8	55.6	0.11	2.1	1.16	0.65	0.93	0.10	0.11	1.88
M1h	1.24	0.54	0.49	3.9	0.88	54.3	1.09	1.63	36.1	30.2	39.3	31.2	29.5	0.8	25.0	1.9	4.8	4.2	0.8	56.1	0.15	2.2	0.95	0.64	0.91	0.10	0.08	1.13
M1i	1.21	0.54	0.50	3.8	0.89	55.2	1.23	1.67	37.0	29.3	38.5	31.3	30.2	0.8	16.2	3.1	4.9	6.2	0.8	55.7	0.15	2.3	1.01	0.64	0.92	0.10	0.06	1.18
M1j	1.26	0.55	0.49	4.0	0.88	54.7	1.16	1.41	37.4	29.5	37.4	31.3	31.3	0.8	18.5	2.9	4.8	4.9	0.8	55.2	0.16	2.3	0.98	0.64	0.92	0.11	0.18	5.62
M2f	1.25	0.54	0.49	3.6	0.91	54.0	1.13	1.54	36.7	30.0	40.1	31.1	28.8	0.8	21.2	2.9	4.8	5.1	0.8	55.8	0.16	2.3	0.97	0.65	1.08	0.10	0.18	3.55
M2g	1.29	0.54	0.48	4.0	0.91	55.5	1.18	1.56	36.5	28.5	37.1	30.1	32.8	0.8	41.7	3.2	5.3	5.2	0.8	56.3	0.14	2.1	1.12	0.63	1.06	0.10	0.18	0.64
M3f	1.24	0.54	0.49	4.2	0.83	55.1	1.45	1.47	39.9	27.5	39.9	31.2	28.9	0.7	184.6	2.0	5.1	4.9	0.8	56.2	0.16	2.0	1.12	0.64	1.04	0.10	0.05	0.88
M3g	1.22	0.54	0.49	4.1	0.84	54.1	1.48	1.66	38.5	26.4	38.7	31.4	29.9	0.7	63.0	2.3	4.9	4.8	0.8	55.6	0.15	2.1	1.02	0.64	1.05	0.09	0.04	1.13
M3h	1.32	0.54	0.47	4.2	0.84	55.3	1.31	1.70	38.3	27.9	38.1	31.6	30.3	0.7	78.4	3.6	5.0	7.2	0.8	56.2	0.15	2.2	1.01	0.62	1.02	0.10	0.07	0.94
M3i	1.20	0.54	0.50	4.0	0.83	56.5	1.42	1.43	38.7	26.1	39.6	31.8	28.6	0.7	75.0	1.8	4.6	4.1	0.8	55.7	0.15	2.1	1.05	0.66	0.90	0.09	0.06	0.98
M3j	1.20	0.54	0.50	3.7	0.87	57.7	1.05	1.58	38.6	28.9	42.4	29.5	28.1	0.7	25.7	2.1	6.1	6.4	0.8	56.0	0.12	1.9	1.11	0.65	0.93	0.10	0.07	0.99
C1a	1.18	0.55	0.51	4.0	0.86	52.4	1.02	1.39	38.8	30.4	37.1	31.9	31.0	0.8	14.5	2.6	4.3	3.7	0.8	55.3	0.14	2.2	1.02	0.62	1.02	0.09	0.12	0.64
C2a	1.26	0.54	0.49	3.0	0.94	58.9	0.86	1.37	41.4	31.8	38.6	31.4	30.0	0.8	12.9	2.6	4.5	4.0	0.9	54.9	0.14	2.2	1.08	0.63	0.88	0.18	0.20	0.38
C3a	1.29	0.54	0.48	3.5	0.90	56.3	1.16	1.12	41.7	29.3	38.2	30.0	31.8	0.7	15.6	3.2	4.7	5.2	0.8	55.9	0.14	2.0	1.06	0.62	0.96	0.22	0.09	0.93
C1b	1.24	0.54	0.49	4.0	0.91	54.1	1.13	1.53	37.2	29.8	37.5	31.6	30.8	0.8	33.3	2.0	5.5	5.0	0.7	55.3	0.11	1.9	1.10	0.63	1.05	0.13	0.18	7.49
C2b	1.25	0.54	0.49	3.2	0.93	52.2	0.73	1.31	35.4	36.0	37.7	31.6	30.7	1.0	35.0	1.9	4.6	4.3	0.8	54.3	0.12	1.9	1.18	0.63	0.97	0.12	0.21	0.24
C3b	1.26	0.54	0.49	3.8	0.87	54.0	1.15	1.38	36.6	31.9	39.1	31.8	29.2	0.9	47.9	3.4	5.0	3.9	0.9	55.3	0.14	2.1	1.03	0.64	0.93	0.12	0.07	0.16
E1a	0.75	2.38	4.81	1.5	0.88	2.4	0.20	0.40	34.0	47.6	28.2	31.4	40.4	1.2	4.8	0.3	0.8	0.2	0.2	29.1	0.95	0.56	2.12	0.50	0.61	0.38	1.26	0.005
E2a	0.76	2.34	4.82	1.6	0.72	3.5	0.16	0.47	32.0	48.7	28.0	31.9	40.1	1.3	4.5	0.4	0.7	0.2	0.2	29.3	0.98	0.56	2.08	0.56	0.64	0.41	1.73	0.006
E2a	0.74	2.22	4.63	1.6	0.98	1.9	0.17	0.51	31.9	49.2	26.9	32.6	40.5	1.3	6.5	0.4	0.9	0.2	0.3	28.1	0.96	0.56	2.24	0.57	0.67	0.49	1.13	0.014
E1b	0.75	2.36	4.92	1.5	1.00	3.0	0.20	0.45	31.8	49.5	26.6	29.9	43.5	1.3	4.8	0.4	1.0	0.2	0.2	28.6	0.95	0.55	2.44	0.55	0.59	0.51	1.60	0.006
E2b	0.76	2.35	4.77	1.7	0.79	4.7	0.20	0.44	32.0	48.8	27.1	28.7	44.2	1.3	8.9	0.4	1.0	0.2	0.3	26.7	0.92	0.54	2.67	0.57	0.65	0.44	1.57	0.015
E3b	0.73	2.23	4.50	1.47	0.89	2.3	0.17	0.56	31.1	49.8	27.1	32.1	40.8	1.34	6.92	0.37	0.94	0.23	0.25	29.5	0.93	0.51	2.77	0.55	0.67	0.49	1.14	0.013

P1 = Pr/Ph, P2 = Pr/nC17, P3 = Ph/nC18, P4 = nC17/nC27, P5 = CPI-1, P6 = DiaSt (%), P7 = St29S/R, P8 = St29I/R, P9 = %27St, P10 = %29St, P11-P13 = %St27-29Iso, P14 = C29/C27, P15 = St29/Tt30, P16 = Ts/Tm, P17 = Hop/Mor, P18 = Dia/NorM, P19 = 29(Ts/Tm), P20 = %22*S* (C31-hop), P21 = Gammacerane-I, P22 = HHI, P23 = Hop(35/34), P24 = MPI(1), P25 =MPR, P26 = Phen/nC18, P27 = DBT/PHEN, P28 = TAS/MAS. The description for these parameters is very similar to those shown in Table 5.6. The samples designated O-, M-, C-, and E- are the original crude oil, 'migrated' oil portions, column (migration) extracts and the rock extract variants respectively.

Resemblance analyses were carried out on the sample subsets to determine the similarity levels between biomarker contents of the 'migrated' oils as described in Appendix IV-e. The outcome of the resemblance analysis was a half-triangular resemblance data matrix whish showed the distance based on the Euclidean option as shown in Appendix IV-d.

Cluster analysis of the resemblance matrix was also carried out. The tree-like structures (known as dendograms) resulting from this test showed how the objects (samples) group hierarchically into clusters and reveal the dissimilarities between the 3 groups of related migration samples based on distances between them (e.g. Bratchell, 1989). A dendogram for the resemblance matrix from the olefin abundances (Appendix IV-b) and selected biomarker parameters (Figure 5.17) revealed some degree of variability between the initial North Sea oils and the 'migrated' portions (M's). This is indicated by general slight decrease in the resemblance between the North Sea oil and subsequent 'migrated' oils variants. As earlier observed in the olefin distribution (Figure 5.11), differences in profile patterns could be attributed to variations in the particle sizes, which are related to their respective surface areas, as well as surface volume available to the oil for 'wetting' even at saturation point. The saturation point, in this case, is regarded as the time at which the first drops of migrated oil emerged after the start of a migration run, with the assumption that the oil would have, first, had contact with (wetted) most of the particles for this to occur. It is believed that the degree and speed of saturation (flow rate) of the column content by the migrating oil are factors that could be greatly influenced by particle size (surface area) and efficiency of the column packings (e.g. Brothers *et al.*, 1991).

Although cluster analysis is less useful where sequential ordering of the samples interrelationship is required, a slight positive variability (increasing distances) across the 'migrated' samples was observed (Figure 5.17). It could also be seen that there is some level of fusing of the 'migrated' oil variants (in terms of similar grain size and order elution of oil portions), first, with each other (e.g. M3f, -g, -h, -i) before amalgamating with similar links and other samples. The implication of this is that the 'migrated' oils are well separated from related members (except the rock extract) especially the original oils even in spite of their close relationships in biomarker abundances. The plot clearly grouped the samples into 2 distinct clusters (North Sea oil-related samples and the rock extracts) and sub-clusters (North Sea oils + 'migrated' oils; 'column' extracts and rock extracts). As expected, the crude oils (O1, O2), 'migrated' oils (M's), and 'column' extracts (C's) do not link to the rock extracts (E's).

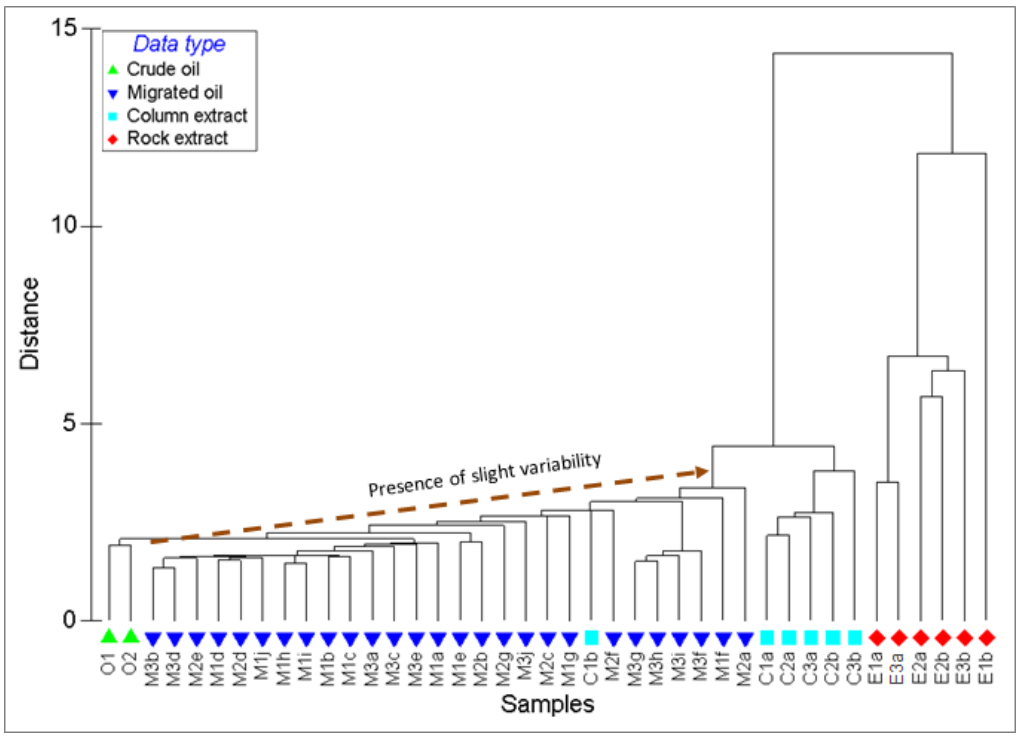


Figure 5.17 A dendogram illustrating the information from the analysis of the resemblance matrix of the olefins and biomarker parameter observations in the lab migration-derived samples. The hierarchical clustering analysis was executed using the single linkage option in Primer6 computer software.

In the case of the fatty acid observations, the dendogram (Figure 5.18) continued to show two major extreme divisions (fresh North Sea oil and column + rock extracts) in terms of their acidic content. Clearly the next main cluster consisting of the 'migrated' oils contain *n*-acids (short-chain) which is believed to be derived from the rock matrix through which they had migrated. However, no trend showing the direction of a decreasing or increasing similarity level between these oils was established, which compares to previous observations in the *n*-acid distribution profiles of 21 'migrated' oil portions (Figure 5.12). The non-detection of hopanoic acids (HA) in the 'migrated' oil portions is reflected in separation of the column extracts from the 'migrated' oils cluster. The clustering of column extracts and rock extracts samples as well as the close resemblance between them is the implication of high abundance of total acids in both sample groups (Table 5.8; Appendix IV-a).

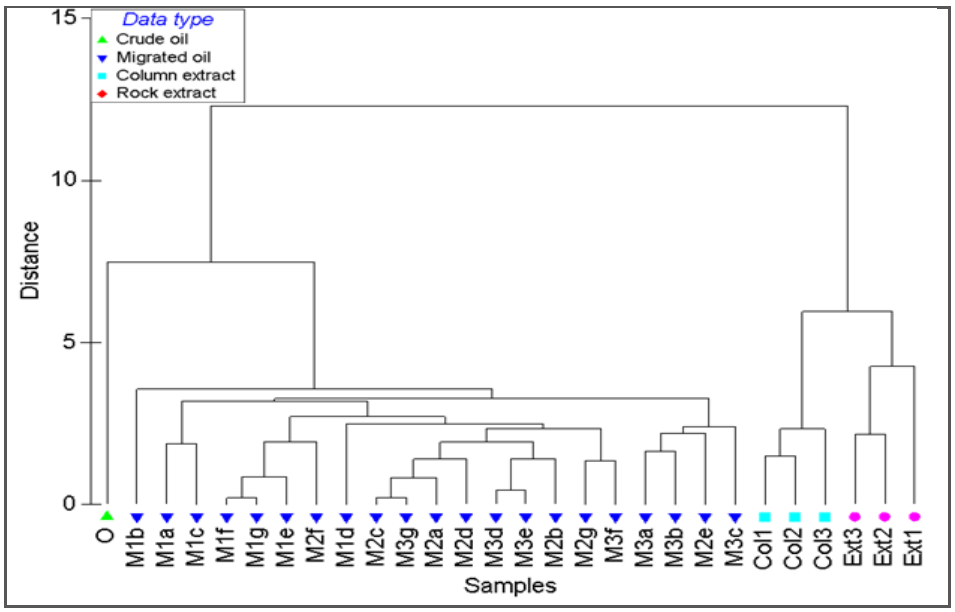


Figure 5.18 Dendrogram resulting from hierarchical cluster analysis of the resemblance (Euclidean distance) matrix for the fatty acid abundances in 28 samples using the group average link variation.

The features of dendograms allow the reordering of samples on the *x*-axis in many possible rearrangements, for clearer presentation and to avoid the branches overlapping each other. However, the reordered results are not unique, and a perfectly sequential ordering (e.g. M1a, -b, -c, …, M1j) is not possible (Clarke, 1993). Going by its name, the cluster analysis' main task is to group (arbitrarily) samples into discrete clusters and does not regard the display of their inter-relationships on a continuous scale. The application of cluster analysis and its representation for the latter may be misleading; hence, the need for an ordination-based analytical method, most commonly, the PCA (Clarke and Gorley, 2006). It is best to use cluster analysis in conjunction with PCA since agreement between both representations should strengthen the confidence in both.

PCA Plots and Marker Relationships

On 41 (replicate) samples consisting of initial North Sea oil (2), 'migrated' oils (27), column (packing) extracts (6), and Kimmeridge extracts (6); 29 chromatographic data variables each of olefins (Appendix IV-b) and selected biomarkers parameters (Table 5.12) were measured. The acid species (32 variables) were measured only for 28 objects in this data matrix subset, and analysed separately by PCA. The problem to be addressed is clear, as listed previously in the study objectives: to determine the extent to which the initial compositions of petroleum have been altered, by these low-concentration compounds, during and after its migration to a reservoir, if such phenomenon occurs, and/or if it is feasible in a laboratory-time scale and conditions.

Large data matrices were converted to a few plots, using the PC method, from which informative deductions were drawn. The PC score and loading plots for all 41 samples and 58 variables (olefins + selected biomarker parameters) are shown in Figure 5.19'a', and 'b' respectively. The Mahalanobis distance plot (Appendix IV-e) for testing outliers, revealed none in the data set. Two features are distinct: 'migrated' oils, column extract and the rock extracts are separated from each other, and the rock extracts are more scattered in the p-dimensional space. This could be due to a distortion of dissimilarity distances caused by a projection of high dimensional data on the two-dimensional plane, and could be greatly improved by plotting the data on a 3D plane.

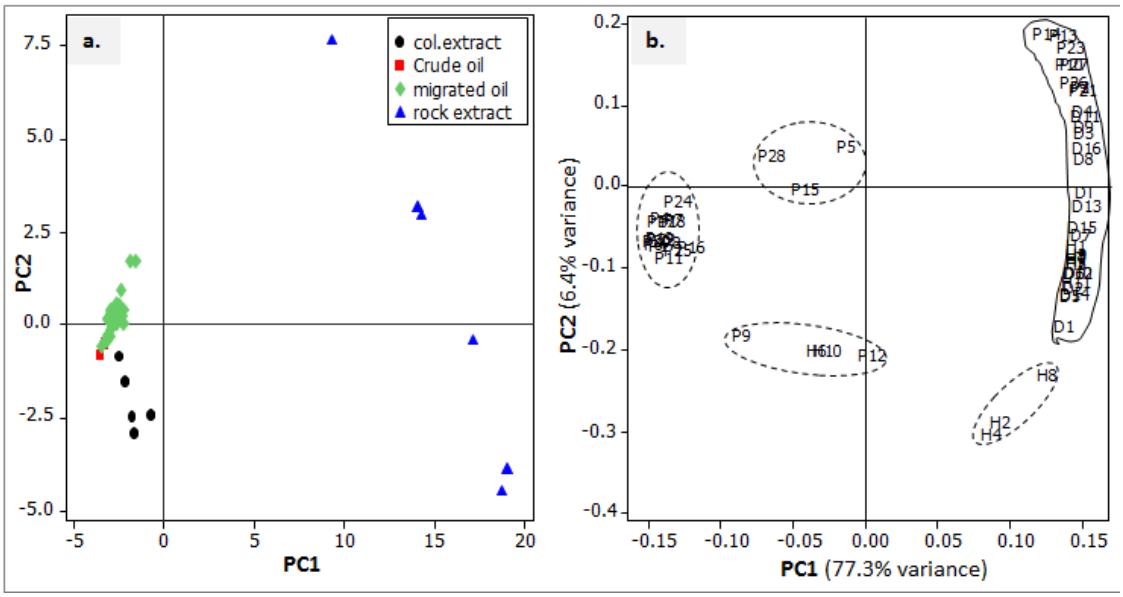


Figure 5.19 Plot of the first two principal components, (a) score and, (b) loading vectors, of abundance of olefins (11 hop-17(21)-ene, H's and 16 diasterenes, D's) present in 'migrated' oil samples, and 28 selected biomarker parameters, P's (Table 5.12) computed for these oils. The values in parentheses represent the % variance for the first 2 principal components (PC1 and PC2) of the loading vectors (olefins + biomarker parameters).

In the loading plot which corresponds to Figure 5.19b, it is easy to directly identify the group of variables that caused the distortion in resemblance distances between the rock extract samples and their clear separation from other samples, as well as those variables that are responsible for the clustering (separation) of the other three classes of samples. The directions in Figure 5.19a, correspond directly with those in Figure 5.19b. The rock extracts are separated both from each other and from the rest of the samples in a vertical and horizontal direction respectively. Hence, variables far from zero in the vertical direction on the loading plot (mainly D1, P9-10, P12-15, P23, H2, H4, H6, H8 and H10; Table 5.11) are responsible for this spread. These variables also account for the separation of the column extracts from the 'migrated' oils, as well as the slight variations between the fresh oils and the 'migrated' oils. Similarly, variables that are horizontally far from zero on the same

loading plot (Figure 5.19b), which include all diasterenes (D's), most hopenes (H's) and all biomarker parameter except P5, P12 and P15, contribute to the separation between the extracts and other sample types. This observation was similar where the bulk loading species (olefins and biomarker parameters) in the above interpretation were analysed and plotted separately (Figure 5.20).

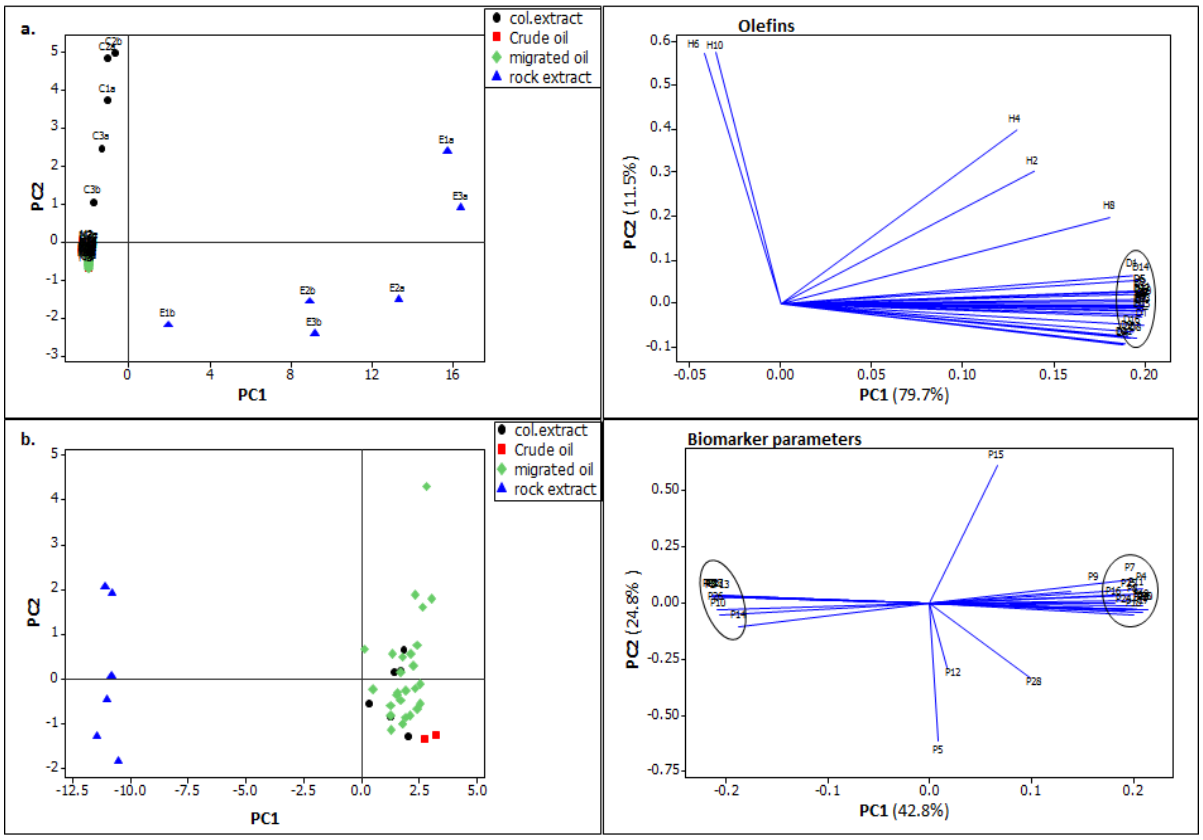


Figure 5.20 PCA score plots and loading plots of a) migrated oil olefins and, b) migrated oil selected biomarker parameters (Table 5.12). Note the similarity in the direction of clusters and samples separation on score and loading plots in both cases. The loading plot of olefin markers and biomarker parameters and first two principal components revealed distinct clusters of co-varying variables. Values in parentheses represent the % variance for PC1 and PC2 of the variables (olefins and biomarker parameters).

The score/loading vector relationship was also applied to the PCA plots of the fatty acid data matrix (Appendix IV-b). Figure 5.21 shows the loading plot (a) and biplot (b) of the first two components of the fatty acid abundances in the migration samples. The four groups of samples were, again, separated in clusters (Figure 5.21b) in the horizontal direction. The species responsible for the separations occur in the same direction of change on the loading plot (Figure 5.21a). Hence, all the *n*-acid variables which are far from the origin (zero) in the horizontal direction are responsible. Similarly, the variability between the 'migrated' oils in a vertical direction is owed to many of the *n*-acid species (A's) and not including the HA's, as these were not detected in the oils in the first instance. The position of the North Sea oil marked it out as an outlier, but this was due to negligible acidic content (zero HA) of the original crude oil (Table 5.8).

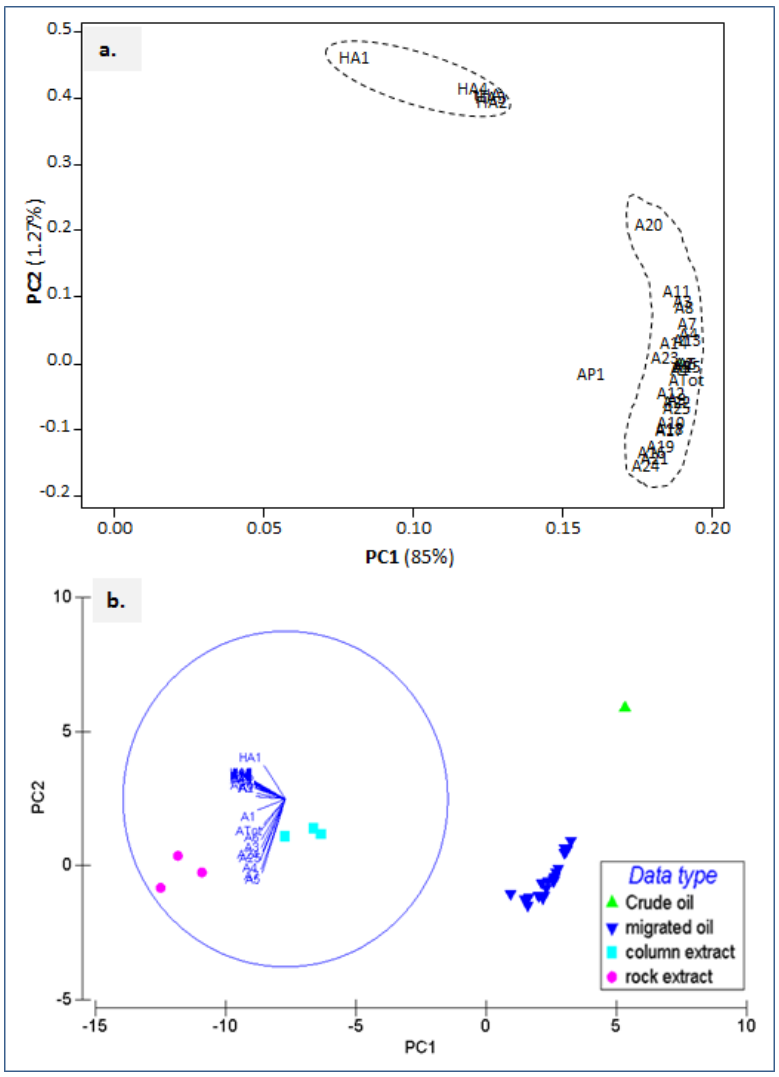


Figure 5.21 Loading plot (a), and biplot (b) of the first two principal components obtained from concentrations of saturated fatty acids present in 'migrated' oil samples (Minitab16 statistical software). Values in parentheses show % variance for PC1 and PC2 of the acidic variables in (a).

Interpretation of Principal Components

The Eigen analysis of correlation data matrix of the PC1 vs. PC2 scores, for the olefin-biomarker parameter and acid variables, is shown in Table 5.13. In respect of olefins and biomarker parameter analysis, the first principal component (PC1) has variance (eigenvalue) 44.087 and accounts for 77.3% of the total variance (Figure 5.19b). The second principal component (PC2) has variance 3.654 and accounts for 6.4% of the data variability. Together, the first two PCs represent 83.8% of the total variability. Thus, most of the data structures, in the present case, are captured in two primary dimensions. The remaining principal components account for a very small proportion of the variability (close to zero) and are probably unimportant. Similarly, in the eigenanalysis of the acid data correlation matrix, most of the variations are captured in the first two PC dimensions with eigenvalues 26.6 and 2.02, respectively, and accounts for 89.3% of the total variance.

Table 5.13 PCA data table of eigenvalues and e*igenvectors* showing the linear combinations of variables making up the first five principal components (PCs) of the olefin/biomarker parameters and acid variables in respective data matrix.

Eigenanalysis of the Correlation Matrix (Olefins and biomarker parameters)

Eigenvalue	44.087	3.654	2.481	1.434	1.133	0.979	0.802	0.520	0.351
Proportion	**0.773**	**0.064**	**0.044**	**0.025**	**0.020**	**0.017**	**0.014**	**0.009**	**0.006**
Cumulative	0.773	0.838	0.881	0.906	0.926	0.943	0.957	0.966	0.973

Variable	PC1	PC2	PC3	PC4	PC5
H1	0.144	-0.097	0.098	0.023	0.026
H2	0.091	-0.314	-0.104	-0.171	0.179
H3	0.144	-0.107	0.094	0.024	0.030
H4	0.085	-0.329	-0.199	-0.085	0.145
H5	0.144	-0.120	0.093	0.027	0.031
H6	-0.034	-0.225	-0.497	0.185	-0.153
H7	0.144	-0.114	0.093	0.026	0.031
H8	0.124	-0.255	-0.007	0.030	0.088
H9	0.143	-0.115	0.096	0.046	0.024
H10	-0.029	-0.225	-0.501	0.191	-0.171
H11	0.142	-0.142	0.094	0.001	0.044
HT	0.144	-0.111	0.090	0.020	0.032
D1	0.135	-0.195	0.090	-0.009	0.073
D2	0.141	-0.149	0.096	0.028	0.040
D3	0.149	0.042	-0.011	0.008	-0.068
D4	0.148	0.069	-0.022	0.006	-0.083
D5	0.140	-0.158	0.090	0.007	0.045
D6	0.143	-0.130	0.041	-0.053	0.030
D7	0.147	-0.083	0.033	-0.023	0.006
D8	0.149	0.009	0.030	0.015	-0.052
D9	0.149	0.048	-0.027	-0.011	-0.070
D10	0.144	-0.129	0.090	0.021	0.031
D11	0.148	0.063	-0.022	-0.007	-0.077
D12	0.144	-0.129	0.085	0.026	0.028
D13	0.150	-0.049	0.011	-0.011	-0.016
D14	0.142	-0.156	0.050	-0.028	0.062
D15	0.147	-0.074	0.065	0.028	0.001
D16	0.150	0.024	-0.011	-0.012	-0.050
DT	0.150	-0.032	0.037	-0.006	-0.019

Variable	PC1	PC2	PC3	PC4	PC5
P1	-0.145	-0.097	0.012	-0.004	0.078
P2	0.147	0.097	-0.011	0.005	-0.079
P3	0.147	0.098	-0.012	0.001	-0.080
P4	-0.143	-0.062	0.130	0.027	0.065
P5	-0.014	0.025	-0.365	-0.532	0.081
P6	-0.147	-0.095	0.015	-0.001	0.042
P7	-0.134	-0.064	0.159	0.031	-0.044
P8	-0.135	-0.094	0.102	-0.016	-0.105
P9	-0.087	-0.209	0.005	0.022	-0.551
P10	0.138	0.126	-0.111	-0.010	0.168
P11	-0.138	-0.111	0.041	0.054	0.080
P12	0.001	-0.230	0.100	-0.323	-0.377
P13	0.134	0.161	-0.063	0.022	0.009
P14	0.123	0.163	-0.090	-0.057	0.333
P15	-0.044	-0.028	0.152	0.495	-0.139
P16	-0.123	-0.099	-0.007	0.051	0.124
P17	-0.144	-0.066	0.054	-0.038	0.080
P18	-0.137	-0.066	0.110	-0.082	0.045
P19	-0.145	-0.086	-0.011	0.030	0.123
P20	-0.147	-0.090	0.025	-0.008	0.086
P21	0.147	0.093	-0.001	0.004	-0.072
P22	-0.144	-0.089	0.011	0.006	0.128
P23	0.140	0.148	-0.042	0.033	-0.117
P24	-0.132	-0.041	0.085	-0.013	0.022
P25	-0.132	-0.101	0.079	0.029	0.028
P26	0.142	0.105	-0.091	-0.010	-0.144
P27	0.141	0.126	-0.025	0.026	-0.128
P28	-0.067	0.014	0.224	-0.473	-0.248

Eigenanalysis of the Correlation Matrix (Acid data)

PC	1	2	3	4	5
Eigenvalues	26.6	2.02	0.744	0.664	0.467
%Variation	83	6.3	2.3	2.1	1.5
Cum.%Variation	83	89.3	91.6	93.7	95.2
Eigenvectors					
Variable	PC1	PC2	PC3	PC4	PC5
A1	-0.17	-0.065	0.135	-0.035	-0.118
A2	-0.18	0.014	0.142	0.024	-0.172
A3	-0.148	-0.243	-0.167	-0.033	-0.7
A4	-0.157	-0.368	-0.176	-0.018	-0.037
A5	-0.143	-0.438	-0.222	0.018	-0.082
A6	-0.148	-0.185	0.402	0.272	0.227
A7	-0.148	-0.417	-0.099	0.079	0.131
A8	-0.187	0.072	-0.019	0.011	0.067
A9	-0.182	0.016	0.018	0.02	0.139
A10	-0.188	0.064	0.018	-0.039	0.076
A11	-0.188	0.081	-0.011	0.032	0.067
A12	-0.192	0.099	-0.011	-0.008	-0.012
A13	-0.189	0.084	-0.011	0.03	0.063
A14	-0.192	0.092	0.009	-0.053	-0.013
A15	-0.191	0.105	-0.01	0	-0.012
A16	-0.192	0.083	0.019	-0.082	-0.011
A17	-0.192	0.095	0.008	-0.049	-0.01
A18	-0.192	0.084	0.023	-0.091	-0.011
A19	-0.192	0.091	0.015	-0.067	-0.01
A20	-0.192	0.092	-0.002	-0.03	-0.014
A21	-0.192	0.083	0.027	-0.1	-0.009
A22	-0.18	0.063	0.045	-0.172	0.007
A23	-0.19	0.104	-0.043	0.067	-0.016
A24	-0.148	-0.289	0.25	0.05	-0.161
A25	-0.139	-0.311	0.371	0.183	0.319
ATot	-0.134	-0.15	-0.592	-0.235	0.468
HA1	-0.131	0.199	-0.313	0.762	-0.046
HA2	-0.191	0.101	-0.02	0.022	-0.021
HA3	-0.191	0.105	-0.025	0.036	-0.019
HA4	-0.191	0.103	-0.028	0.041	-0.021
tHA	-0.191	0.108	-0.028	0.044	-0.019
AP1	-0.18	0.035	0.155	-0.406	0.01

Other Hydrocarbon and Biomarker Compounds

The PCA was also extended to regular saturated biomarkers (*n*-alkanes, steranes and terpanes) data matrix (Appendix IV-b). The objects (samples) included replicate North Sea oils (2 x 'O's), 'migrated' oils (2 x 24'M's+'R's), column extracts (2 x 3'C's) and replicate rock extracts (2 x 3'E's).

The degree to which each variable contribute to the principal component as well as the relationships between the samples and variables are shown using the score plot and loading plots (Figure 5.22). The three related classes of the migration samples (fresh oil, 'migrated' oils and column extracts) were generally clustered together while the first run samples are clearly separated from the duplicate samples. The variables responsible for this difference are spotted on the loading plot following the same direction of separation on the score plot. These are the biomarkers that plot away from the origin in a vertical direction, and include most biomarkers, but largely steranes. In the horizontal direction, the rock extracts, also in a cluster, are markedly separated from the rest of the clusters, and the variables that were far from zero horizontally (all except 28ββ*S*, 29ββ*R* and 31*R*hop) could be responsible for this separation. With respect to changes in the composition of these compounds resulting from migration, again, it is not very clear but an increasing trend could be observed from the original oil to the migrated oils on the score plots for both runs (Ms and Rs).

The normal alkanes and all biomarkers clustered at the positive end of the PC1 axis (Figure 5.22b) strongly influencing this component. Likewise, variables 27αα*S*, 28ββS&*R*, 29ββ*R*, 31*R*hop and 29Ts mostly influence PC2. Four major variable clusters, with similar PC1 and PC2 loadings, were observed (Figure 5.22b). The variables within a cluster co-varied with respect to the first PC's, a strong indication that they have similar characteristics (e.g. common source). All biomarkers display high (positive or negative) loadings on corresponding PC indicating a strong influence on that component. No minor influence by any of the biomarkers was observed since none of the variables plotted close to zero on the PC axes. The score and loading plots have, therefore, been used to illustrate the interrelationships between the samples in the analysis and identify the presence, though not conclusive, of some degree of variability across 'migrated' oils.

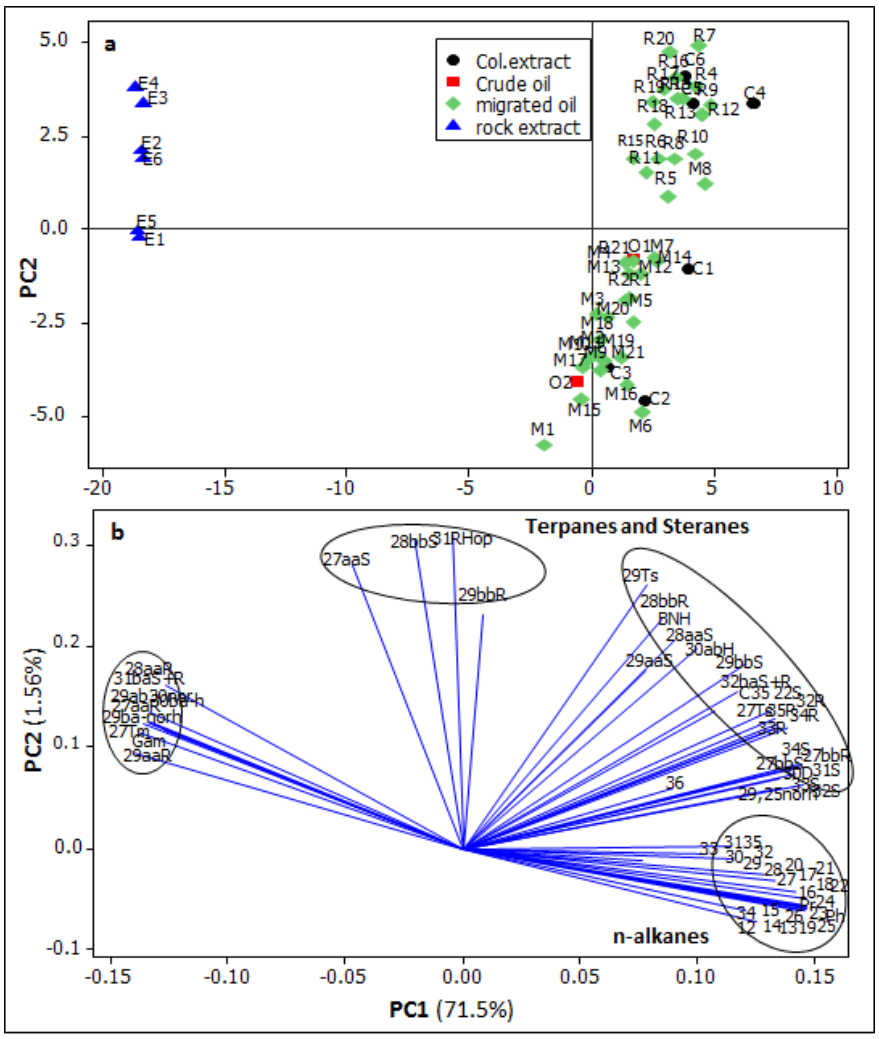


Figure 5.22 PCA score plot, (a), and loading plot, (b), of PC1 vs. PC2 obtained from abundance of saturated hydrocarbons (normal alkanes, steranes and terpanes) present in 'migrated' oils. Both components jointly account for 73.06% of total variability in the dataset (PCA data for saturate HC variables in Appendix IV-d).

5.2.5. *Compositional Variability*

Figure 5.11 showed a general increase in abundance of the olefin compounds from the first to last 'migrated' oils. The consistent but varying trends in olefin abundances and redistribution of the *n*-acid homologues (Figure 5.11 and Figure 5.12) exhibited by the 'migrated' oils which eluted through three different particle-sized solid phases suggest that concentrations and distribution of migrated oil compositions may be affected, not only by the organic richness of the rock that they migrate through, but also by the effects of other properties such as surface area, cement, porosity and permeability. Again the estimated BET surface areas of the particles (Table 5.3) were not proportional to grain size of the particles; this may be due to differing void volumes created by different sample particle in the sampling tube (surface area analyser) discussed earlier in this chapter. It is thought that the

same mechanism that operated between the dosing gas and rock pore surfaces in the determination of the adsorption isotherms for surface areas of the rock samples are, in effect, similar to the oil-rock matrix interaction during migration. An implication of this behaviour could explain observed unexpected differences in olefins and acid concentration in the corresponding extracts of the three rock variants. The effect of particle size variation on the concentrations of detected aliphatic and aromatic compounds appeared to be negligible. This implies that the distribution of low concentration compounds such as the olefins and acids in crude oils are easily 'upset' by a slight change in their concentration due to migration-contamination. The aliphatic and aromatic compounds do not noticeably react to this change due to their usually high concentrations in petroleum (cf. Jaffé and Gallardo, 1993).

Although the PCA technique has proven to be a more useful tool in the multivariate analysis of a higher-dimensional data set (≥30 variables) as in the present study, it should be noted that the interpretation of the PCs is subjective. However, obvious useful PC patterns which are very interpretable were developed and have been applied to the sample data to establish expected variability of sought migration markers within suits of laboratory 'migrated' oil samples.

5.2.6. *Conclusions*

Molecular olefin and acid data, supported by bulk biomarker data relationships, were analysed and interpreted with the aid of a multivariate statistical technique (PCA). Variability in the concentrations and distributions of the marker compound between the 'starting' oil and the 'migrated' portions in controlled laboratory migration experiments were observed.

The main findings of the present simulated migration study include:

The artificial migration of aliquots of a North Sea crude oil (NSA03) through fine to coarse-sized particles of immature, organic-rich Kimmeridge Clay mudstone resulted in changes in the concentration of the olefins and *n*-acids in the 'migrated' oils with increasing migration and this was thought to be due to the solubilisation effect of the light crude oil on the organic content of the clay samples.

The experimental data presented indicate that there is a fairly substantial amount of contamination born by the original North Sea oil during migration. This observation was very apparent with the olefins but tentative in the case of the fatty acid compounds.

The effect of migration through different rock bed volumes due to varying rock particle sizes was demonstrated by comparing profiles of olefin, acid and other regular saturate and aromatic compound distribution between corresponding ‘migrated’ oil variants. Evidence suggests that indeed different porosities caused by these variations play significant roles in the effectiveness of present migration phenomenon. However, differences between migration runs through the same solid phase may, partly, reflect the slight, but unavoidable differences in packing individual HPLC columns (Table 5.9).

The changes in compound composition are reproducible outside factors that cannot be controlled under the laboratory condition. Despite the low levels of solid phase activity and short migration distances (25 cm) employed in this study, the results indicated altered trends in the olefin and acidic biomarker concentration and distribution of a crude oil, the North Sea oil in this case.

With respect to evaluating the extent to which initial saturate and aromatic contents of the migrated crude oils have changed, results show little redistribution effect with insignificant enrichment among some saturated compounds. Because the concentration of aromatic hydrocarbon could be relatively high in crude oil, the redistribution effect due to minor compositional alteration is still insignificant for this group of compounds, but generally more profound in aromatics than in saturates.

This work illustrates the importance of laboratory simulation of petroleum migration under controlled conditions as a reasonable approach for the investigation and assessment of such complicated process as migration-contamination using rare, low-abundance marker compounds. It also portrays the utility of PCA for depicting very small changes within highly complex dimensional data.

Chapter 6 Conclusions

6.0. Introduction

This study was carried out to investigate the potential of rarely reported organic compounds, particularly olefins and carboxylic acids in oils as markers of migration-contamination, believed to occur in many reservoired petroleums. The recognition of such migration-contamination is important in order to understand oil source and maturity assessment anomalies resulting from using only well-known biomarkers in these petroleums. There were two parts to this study; the first involved investigation of possible migration-contamination markers in a suite of Tertiary oils, sampled from reservoirs in the field, and the second consisted of laboratory simulated migration experiments. These laboratory migration experiments used particle size variants of an immature, organic-rich Kimmeridge Clay mudstone abundant in the desired markers, and a mature, Jurassic marine-sourced North Sea oil (NSA03) as the solid and liquid phases respectively, in a steel HPLC column set-up.

6.1. Field Study Samples

The Beaufort-Mackenzie Delta oils, separate into two groups: those sourced from shale of Type II/III kerogen with some higher plant organic matter input; and the other group sourced from predominantly marine sediments with high algal input. Similarly, oils of the Niger Delta in this study were classed into two end-member groups: the mainly terrestrial; and the mixed (marine/terrigenous) oils, a reflection of mixed accumulations and generation from pro-delta shales. Based on the biomarker data of the three studied oil/gas condensates of the Kutei Basin, the source rocks from which they were expelled may have been deposited under highly oxic environment from where it received abundant terrigenous higher plants organic input. This is evidenced by similarities in their hydrocarbon composition, high C_{29}- steranes, high oleanane index and high Pr/Ph ratios (>10) in the oils. These characteristics are typical of deltaic oils that are sourced from Tertiary coaly shale of predominantly terrigenous organic matter. Generally, maturity parameters showed the oil set to be early mature to mid-mature.

6.1.1. *Olefins and Carboxylic Acids in Study Oils*

The investigation of the field study samples confirmed the occurrence of various classes of olefins including normal alkenes, diasterenes and triterpenes (hopenes and oleanenes)

in variable concentrations. Although their concentrations were generally low and variable throughout the sample set, their detectable quantities in oils that had clearly attained thermal maturity sufficient for oil generation, suggested a secondary origin in many of the samples. The occurrence of oleanenes was shown to be prominent in Tertiary oils and/or those containing relatively high amounts of oleanane but very low to absent in other Paleogene/Cretaceous oils. However, correlation assessment of the various isomer pairs such as 18α-olean-12-ene and olean-12-ene versus olean-13(18)-ene, in the sample set revealed the likelihood that these supposedly source-derived olefins (e.g. Eneogwe *et al.*, 2002) may be partly migration-derived. Nevertheless, other olefins found in many of these oils were considered to be derived as a result of migration-contamination, as implied by the presence of other olefins, such as diasterenes and hopenes (Figure 4.22), characteristic of immature organic matter as well as the following non-biomarker indices: non-correspondence of C_{14}-C_{26} carbon number *n*-alkene homologues, to those of the *n*-alkanes, the difference in the carbon preference indices (CPI) and odd/even predominance (OEP) numbers in the linear homologues of most samples (Figure 4.27).

Normal, as well as hopanoic, acids were identified in nearly all the oils. Strong preference for short-chain *n*-acids (SCA, C_{12}-C_{19}) compared to long-chain acids (LCA; C_{20}+) was observed in predominantly marine oils. Terrestrial and mixed oils were characterised by intermediate distribution of both SCA and LCA in which unimodal distributions are prominent. All saturated fatty acids had marked even over odd carbon number predominance (OEP<1). Based on C_{28}/C_{18} ratios, the LCA were most probably derived from leaf waxes of land plants and this is the most likely explanation to why some of the Niger Delta oils are characterised by relatively high concentration of *n*-acids within the sample set. Generally, oils having high levels of terrigenous organic matter correspondingly showed high concentrations of normal acids (Table 4.11).

The distribution of the C_{30}-C_{33} hopanoic acid (HA) isomers revealed the ββ isomers as the most prevalent isomer in all acid-containing oils. These isomers (ββ) are immature and the least stable of the HA isomers; hence, their prevalent abundance in the seemingly mature case study Tertiary oils implied that the immaturity of HA did not alter routine maturity biomarkers in the oils. In addition, high abundances of the C_{31} and C_{32}-HA homologues were consistent with the abundance of acids in oils from Tertiary petroleum settings. In the *n*-acids, even-numbered carbon chain lengths tend to predominate as

opposed to an OEP≥1 for the *n*-alkanes. Similarities in OEP curves for *n*-acids between samples suggest a common origin (e.g. Niger Delta; Figure 4.46) (Scalan and Smith, 1970). Overall, the outcome of the present study on petroleum acids suggests that migration-contamination was a major influence on the acid content of the Tertiary oils. This conclusion was based on the high abundance of carboxylic acids in many undegraded oils, particularly, of the Niger Delta; measured high CPI values of the *n*-acids; and low maturity HA isomer distributions within the mature oils. These are indication that the acids were taken up from adjacent immature organic rock during oil migration, and that maturity of the HA (very low) and the bulk maturity of the oil (relatively mature) are independent of each other within the oils.

6.1.2. *The Reference Oil Samples*

The field 'reference' oils were chosen, for comparison with the key Tertiary oil study set based on dissimilarities in source rock type and age, maturity and general geological setting. This sample set contains two mixed and three predominantly marine-sourced oils. Their acidic and olefinic content compared to those of the case study oils form the basis for their selection. The Trinidad oil (TRO01) and one of the North Sea oils (NSA02) are comparable to most of the terrigenous oils throughout the study; hence, they are believed to originate from mixed (marine and terrestrial) sources. The other reference oils are predominantly from marine organic matter, and are distinguished by their lack of oleanenes, low diasterene content, negligible amounts of short-chain *n*-acids (SCA) and absence of hopanoic acids (HA). These notable differences indicated that the reference samples are mature oils which had probably not travelled through immature organic-rich rocks during their migration and accumulation, and therefore may have not undergone migration-contamination. These observations reinforced the inference of migration-contamination on many of the case study Tertiary oils.

6.2. Laboratory Migration Study

The laboratory-simulated migration study was undertaken in order to determine whether the migration of a mature, Jurassic marine-sourced North Sea oil (NSA03) through an immature organic-rich Kimmeridge Clay mudstone of varying particle sizes would reveal any detectable changes in the concentration and distribution of certain rare markers and if the extent of this change was affected by these size differences. Olefin and acid analysis

of the Kimmeridge Clay extracts showed that it contained relatively abundant olefinic and carboxylic acid compounds and these attributes made the effects of migration-contamination readily recognizable.

6.2.1. *Compositional Differences in Laboratory-Migrated Oils*

The olefinic hydrocarbons detected in the migrated crude oils included the hopenes, disaster-13,17-enes and the methyl-diasterenes (4β-Me-10α-diasterenes). The abundance of olefins and distribution of carboxylic acids observed in the 'migrated' oils were compared with those of the original oil and the three rock extract variants for possible changes in the concentration and distribution of these compounds. The abundance profiles plotted for the olefins of the migrated oils (Figure 5.11) showed generally increasing concentrations of the olefins over an approximately six-hour time scale of the migration experiment. Although these changes were gradual and unsteady across the migrated eluents, consistent abundance and distribution trends for migrated oil samples that were passed through the three particle size variants (coarse, medium and fine) were clearly observed. However, olefin profiles in the eluates of the 'fine' particles were different from those of the other two variants (coarse and medium) for each class of olefins studied. These distinct patterns were consistently shown by the oil samples that migrated through the fine-sized particles for all three olefin groups (Figure 5.11).

Despite the high concentration of *n*-acids and hopanoic acids observed in the clay extract, only short-chain *n*-acids (C_{12}-C_{18}; SCA), maximizing at either C_{16} or $C_{18,}$ were detected in the migrated oils. The concentration profiles represented in Figure 5.12 showed no clear distribution trends since both normal and hopanoic acids were, respectively, very low and below detection limit (<0.25 μg/g) or absent in the initial oil prior to the simulation runs, the concentration of *n*-acids in the oil appears to have been enriched during migration through the acid-rich rock particles. It is not clear why the hopanoic acids were not solubilised by the migrating oil but adsorption and polarity differences may have resulted in the retention of hopanoic acids by the rock matrix. The effect of the different particle sizes were not as apparent as those exhibited by the olefins but the *n*-acid (SCA) profile of the oils that migrated through the finest (<63 μm) rock particles, was again different and showed a more defined distribution than the profiles from the other two size fractions (Figure 5.12). This observation supports the suggestion that small

changes in the conditions (e.g. source rock porosity, permeability, grain size, organic content) of a migration system can affect the extent of migration-contamination (e.g. Bonilla and Engel, 1988).

Principal component analysis was used with cluster analysis to assess the variability between the original crude oil and its 'migrated' portions in order to establish the incidence of migration-contamination in a laboratory simulation experiment. The relationships between the analysed post-migration portions of the North Sea oil, in terms of their variable olefinic and acidic contents, as shown in corresponding PC plots indicated differences between successive eluates as considerable evidence of migration-contamination. This was indicated by best lines of fit between the original oil and its 'migrated' portions (e.g. Figure 5.19; Figure 5.20; Figure 5.21).

6.3. Implication of Findings

Oil-source rock correlation assessments often rely on the presence and distribution of certain molecular markers in crude oils and sediments. Hence, the occurrence of relatively low-abundance olefins and carboxylic acids in crude oils provides another approach to correlating oils to one another, their source(s), and their migration routes, in addition to the commonly used saturated hydrocarbons.

As more olefin/acids-containing oils are recognized, the distributions rather than the presence of these compounds will become distinctive criteria for correlations. Quantitative results from this study have shown that their distributions differ considerably in oils within a single sedimentary basin. Such distributional differences, in addition to correlation applications, may provide important information about their origins. For instance, the Niger Delta oils have been shown, throughout the study, to be similarly distributed in their sources, but contained olefins and acids with largely varying proportions. Distributional differences of this kind is a strong indication of their presence due to post-source (migration alteration) origin which may be partial or complete with possible multiple migration pathways and accumulations.

The occurrence of post-source derived olefinic and acidic markers and the results of this study should find direct application to on-going petroleum exploration activities to bring about a more effective and reliable assessment of oil-source correlation data particularly in Tertiary deltaic settings where reservoired oil is known to have migrated vertically,

typically over a long distance, through thermally immature organic-rich sediments. This means that oil correlations studies which have been previously based on the 'oil from source' theory, and routine (usually abundant) biomarkers whose concentration and redistribution are not perceived in altered oils, could now be more precise when the use of routine biomarkers, which could be derived from source rock, migration path or within the reservoir, are supported by more reliable, mainly non-source derived, low abundant markers such as the olefins and carboxylic acids.

6.4.Limitations of Study

6.4.1. *Field Sampling*

A larger number of samples would have enabled a fuller assessment of migration effects in the oils of the studied basins. Also, a wider assessment of the findings of this work as it relates to migration-contamination in the Tertiary petroleum systems of the world would have required samples from a wider range of basins.

6.4.2. *Migration Markers*

Although using the presence of particular olefins to infer the occurrence of migration-contamination is relatively straightforward, it should be noted that not all olefins in crude oil are migration-derived. For instance, oleanenes and ursenes in oils from Nigeria, Alaska and Canada are thought to be source-derived (e.g. Eneogwe *et al.*, 2002). There is thus a need to employ other low-concentration markers to confirm these claims. However, the extraction, separation and analysis of carboxylic acids from all the samples in this work posed another limitation to this work as the procedures are very time consuming.

6.4.3. *Laboratory Vs. Natural system (subsurface) migration*

The limitations of the laboratory simulation study are mainly the short time scale, and the intensity/type of interaction between the oil and surrounding elements, compared to those of the natural sub-surface oil migration processes. Experimental evidence (e.g. Carlson and Chamberlain, 1986) indicates that in natural (water-wet) systems, geochromatographic processes involving liquid mobile phases will result in compound class compositional changes only. However, molecular fractionation of individual

hydrocarbon compounds, as observed in water-free, liquid-solid laboratory systems is usually quenched in the presence of water and an extrapolation of these results to natural systems is difficult. In other words, lab-based simulations may not account for the effects of water-oil-source rock interactions on the distribution of acid in petroleum, as they occur in natural systems where oil migrates through water-saturated carrier beds.

When the rocks are water-wet, limited opportunity is provided for mineral surfaces to effect any form of separation, and this explains, in part, why field studies show little compositional fractionation due to migrational effects (Trindade and Brassell, 1992). The aqueous environment facilitates the preferential loss of the more water-soluble gasoline range hydrocarbons, which can be lost into solution by water-washing during migration. The solubilities of hydrocarbons decreases with increasing molecular weight but the order of compounds removal by water-washing in lab simulations does not exactly correspond to their relative solubilities (McAuliffe, 1979, Lafargue and Barker, 1988). An explanation for this may be that water washing is often associated with oil biodegradation which normally overwhelms its effects in nature (Connan, 1984). These effects are, however, dominant in the reservoir and does not appear to be noticeable during petroleum migration from source to trap (Lafargue and Barker, 1988). Other influences on the degree and type of interaction of migrating petroleum with pore waters and resultant retention or removal of soluble compounds include migration routes (vertical or lateral); the mineralogy; and the adsorptivity of relevant stationary (mineral) phases (Brothers *et al.*, 1991, Krooss *et al.*, 1991, Trindade and Brassell, 1992). These can represent important input parameters for oil migration models. Substantial experimental effort is still required to investigate and quantify these interactions, particularly with respect to the polar (non-hydrocarbon) petroleum components such as the carboxylic acids. Some suggestions addressing these limitations are given in the following section.

Finally, the simulation of migration should be viewed as a complementary approach for elucidating the effects of natural chromatographic processes on the distribution of organic compounds in crude oils. The advantages of laboratory simulation include the avoidance of maturation, biodegradation and mixing phenomena that may complicate the study of migration effects in natural settings (Bonilla and Engel, 1988).

6.5. Suggestions for Future Work

6.5.1. *Field Studies*

Migration-contamination investigations preferably require evaluation of like pairs of hydrocarbon samples from same basin, one with suspected migration-contamination and one without. Analyses of a crude oil for indication of migration-contamination along with high quality core specimens of its representative regional source rock, and carrier bed along which it migrated would provide the best samples for such a study, but in practise these may be very difficult to obtain.

Non-hydrocarbon compounds often constitute a large fraction of oils but are seldom reported due to their limited applications in petroleum geochemistry (e.g. Galimberti *et al.*, 2000). This may be largely due the often laborious and time consuming procedures undertaken in their analyses. Their routine application is believed to have great potential for enhanced interpretation of migration processes because they have been observed to show changes in their concentrations and distributions in petroleum (e.g. Larter *et al.*, 1996). Some well-known NSO compounds reported in literature include carbazole, quinoline, carboxylic acids, ketones, esters and phenols (e.g. Jaffé and Gallardo, 1993, Clegg *et al.*, 1998, Taylor *et al.*, 2001, Lucach *et al.*, 2002). The present study has applied one of these polar compounds (carboxylic acids) in detecting migration-contamination and found it applicable. It is believed that the effectiveness of this group of compounds lies in the ease by which they are extracted from the containing specimen, which in turn minimises contamination (usually *n*-acids) associated with handling during the analyses. These contaminants, as little as could be present (Figure 4.43), sometimes, override the actual acid content of the samples, especially in samples with concentration below 20ppm or just above detection limit (~0.5ppm). Hence, it is recommended that development into new methods for analysing carboxylic acids and other NSO compounds that require lesser preparative procedures should improve their applicability as migration indicators. An example of such recent development in analytical methods is the Fourier Transform Ion Cyclotron Mass Spectrometry (FTMS) for the characterisation and application of NSO compounds in petroleum, resulting in a new branch of petroleum geochemistry called “petroleomics” (e.g. Rodgers and Marshall, 2007). Routine application using new methods would promote continuous improvement in the knowledge of migration factors.

6.5.2. *Laboratory-Simulation Studies*

Migration simulation has been acknowledged as a more practicable approach, than obtaining field samples along a whole migration pathway, for assessing the incidence and effects of migration-contamination. The present study, having applied this laboratory approach, has shown results which revealed clear indications of migration-contamination but also several inconclusive observations. This may be as a result of the necessarily unrealistically fast time scale on which the laboratory migration study operated compared to sub-surface field scenarios and also the relative simplicity of the laboratory studies.

Hence, further investigations could be designed to include longer experimental time-scales, with adjustments of various system parameters to monitor the effects of various levels of important oil and rock attributes such as maturity, acidity, viscosity (oil), mineral phase (rock) lithologies, water saturation, grain size, porosity, permeability, and adsorptivity. It is also important to consider the influence of the properties of the mobile phase (oil) components, such as polarity, molecular weight and chirality, on the adsorptivity of the various mineral surfaces when exposed to these components. The adjustments should provide better control on the physical conditions (and the factors they affect) of the setup, which includes system pressure, temperature (and its oil viscosity relationship), column length (migration distance/time), and column internal diameter (capillary pressure, flow rate, direction of flow). There are considerable differences in the extent of these conditions between the laboratory and field scenarios. These can be manipulated in a laboratory simulation to mimic to some extent, those observed in a natural migration system. For instance, the effects of various lithologies of the rock matrix and migration distances within the carrier beds can be monitored by varying the percent composition of clay (e.g. montmorillonite) in the mineral phase, and the column length (migration time and distance), respectively. A set of more than two factors and/or sample attributes could be varied and observed within one set-up. It is believed that actual field processes can be better extrapolated based on the results of such laboratory-study improvements, and given that the evaluation of the effects of migration in real systems could remain complex, further laboratory simulation studies are recommended.

In addition, further studies on the implications of olefins and acids, and other often less studied rare components in petroleum should boost their routine application thereby increasing the number of available and supplementary tools for addressing many of the

petroleum assessment and development challenges faced by the petroleum geochemist and the petroleum exploration industries.

6.6.Considerations for study aims and objectives

This project has addressed questions raised in the course of a review of the importance of the research topic. Most of the objectives set out initially to answer these questions and thus the main aim of the research and the study hypothesis (Section 1.5) were achieved. This section contains brief discussion of how each of the listed objectives (Section 1.6) was met, and the extent to which prior research questions were addressed (Section 1.5).

Field samples from 3 typical Tertiary deltaic petroleum regions were obtained. However, samples of more (perhaps up to 5) Tertiary deltas and obtaining more samples in each region would have provided a wider range of data for better comparisons and informed inferences.

Olefins and carboxylic acids were successfully analysed and quantitated from most of the study samples, and their relative abundance and distributions were used to determine the incidence of migration-contamination in these samples within their respective basins.

Simulated migration experiments were carried out using a sample of Kimmeridge Blackstone as the immature organic-rich rock through which an oil was migrated, and a North Sea oil (NSA03) as the liquid (mobile) phase. Oil was passed through varying particle sizes of the solid mineral phase, and portions of migrated oils were collected at regular time intervals.

Biomarker analyses were carried out on these migrated oils and changes in distribution of the routine biomarkers and selected olefins and acid markers were recorded. The extent to which these changes occurred in the migrated portions along the column, with time, was determined by changes (or lack of them) in the concentrations of the various components in these oils.

Acidic (linear and hopanoic) compounds were present at varying, but low, concentrations relative to saturated and aromatic hydrocarbon biomarkers. The outcome of the simulated migration experiment revealed that minor disturbances or changes to the migration system has profound effect on the distribution of acid homologues in the altered oil.

Extensive amounts of data for case study oils from 3 petroleum basins were generated. A data set that would be more useful in distinguishing worldwide Tertiary petroleum would have to include more of such petroleum systems, hence, the present research data alone could not meet this objective but could be the basis of such a database for this purpose in the future.

Ultimately, the mechanism of migration-contamination has been better clarified using a simplified laboratory simulation experiment. Olefins, carboxylic acids, and, perhaps, other low-concentration markers, could be used as evidence of migration-contamination due to their level of rare occurrence and abundance in petroleum but abundance in thermally immature, organic-rich sediments. However, their application as migration markers must first rule out other equally influential factors such as thermal immaturity and biodegradation. The extent to which the migration-contamination phenomenon occurs in all Tertiary deltaic basins is not completely defined by the outcome of this study. It could be that the evidences of this process could represent only a part of the whole source of a particular contaminant (e.g. oleanenes could have been both source- and migration-derived). Migration-contamination is quantifiable in a general sense, and this was achieved by comparing differences in concentrations of both test mobile phase and rock extracts with those of the migrated oils. This approach, as with the simulated migration itself, is very simplified, and did not account for other factors and migration processes that may either be accentuating or depleting targeted components in the migrated samples. Precise measurement of the level of contamination of petroleum within a migration system will need to consider the significant factors outlined within an appropriate mathematical model.

It is an established fact that the occurrence of unusual biomarker distribution in petroleum does not always indicate migration-contamination, and it is also easy to infer such process where favourable conditions seem to have been met by the hydrocarbons in question. It should however, be remembered that migration is complicated and misinterpretation of migration effects based only on the occurrence of unusual biomarkers could result in huge commercial loss to the oil exploration and production companies and to minimise the risk of such a situation will require that as many tools and approaches as available are used.

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APPENDICES

Appendix I-a

List of all chemical standards used during execution of work plan and their sources.

Standard	Formula/ MW	Properties/ reagent grade	Sample fraction	Procedures/ analytical tech.	Supplier/ source
Squalane	$C_{30}H_{62}$; MW: 422.83	99%; Bp: 210-215^{o}C; mp: 38^{o}C	Saturated HCs	Surrogate std., SARA/ GC, GC-MS; TLC ref (sats) standard	Aldrich, UK
1,1'-binaphthyl	FW: 254.33	98%; Light brown powder	Aromatic HCs	Surrogate std., SARA/ GC, GC-MS	Avocado Resources Chem. UK
n-heptadecylcyclohexane	$C_{23}H_{46}$; MW: 322g/mol	White powder	Saturated HCs	Internal quantitation std., GC, GC-MS	ICN Biomedicals Inc. UK
P-Terphenyl	$C_{18}H_{14}$; MW: 230.31g/mol	99%-UV; mp: 212-213^{o}C, irritant, white crystalline powder	Aromatic HCs	Internal std/ GC, GC-MS	Fluka Chemie, UK
5α-Androstane			Saturated HCs; Olefins	Internal standard; GC, GC-MS	Fisher scientific
Cis-2-Methyl, (Z)-7-Octadecene	$C_{19}H_{38}$; MW: 266.51g/mol	Liquid; other info n/a	Olefins	Internal quantitation standard; GC, GC-MS	Sigma-Aldrich UK
5β-cholanic acid (Ursocholanic acid)	$C_{24}H_{40}O_2$ MW: 360.57 g/mol	Solid white granules; other info n/a	Carboxylic acids	Surrogate standard; aqueous ion exchange acid extraction	Sigma-Aldrich UK.
1-phenyl-1-cyclohexane carboxylic acid	$C_{13}H_{16}O_2$ MW: 204.27g/mol	95%; odourless Beige, Solid Powder; mp: 119 - 124°C	Carboxylic acids	Internal quantitation standard; GC, GC-MS	Acros Organics
n-tridecyl-benzene			MAS band	TLC ref standard	lab
Anthracene			TAS band	TLC ref standard	Sigma
Eicosane / tetracosane	*n*-$C_{20}H_{42}$; MW: 282	99%; solid waxy white crystals; irritant	SHC band	TLC-Ag^{+} ref standard	Aldrich
Tetradecene			Olefin band	TLC-Ag^{+} Ref. standard	lab

Appendix I-b

List of main materials and chemicals used to carry out the acid extraction and analysis.

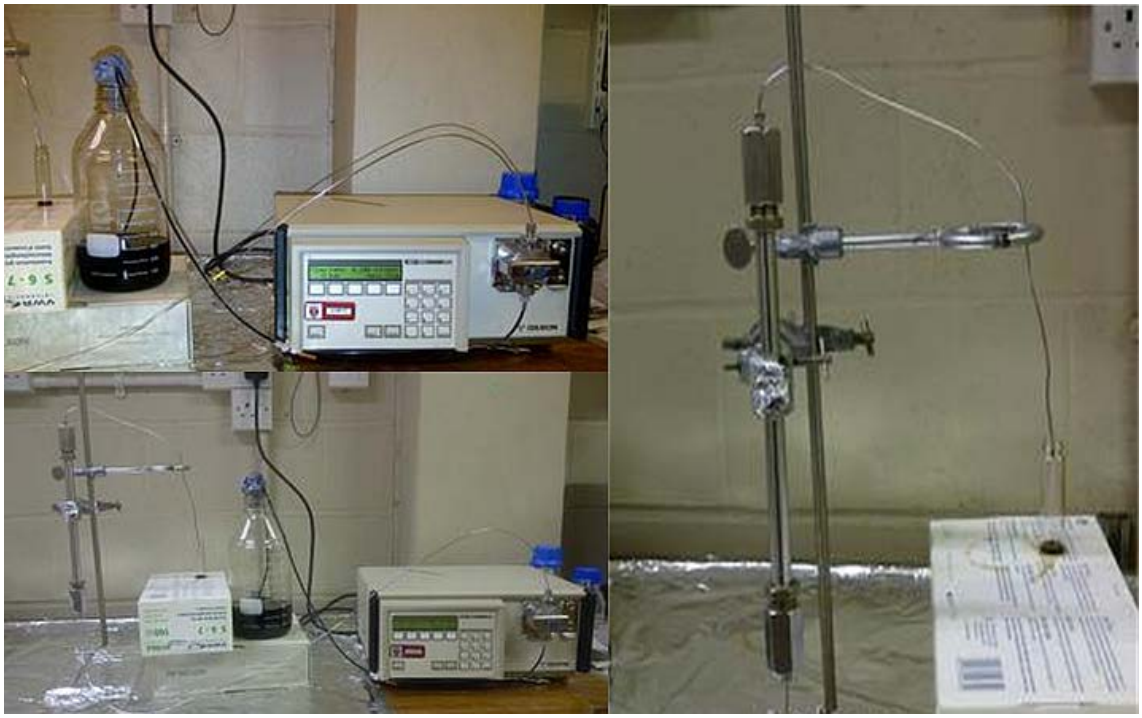
Glass wares:	10ml glass vials Beakers (50ml) 10/50ml measuring cylinders 100ml RBFs 6ml plastic columns 500ml separating funnel Quick fit test tubes Column adaptors 6ml columns and reservoirs Liquid column separating columns (30cm, 1cm id) 5µl and 10µl micro-syringes Glass pipettes
Chemicals/ Materials	Anhydrous sodium sulphate (Na_2SO_4) Alumina/ silica gel 6ml-4g SAX-SPE column Silica glass cartridges 5β-Cholanic acid (surrogate standard) phenyl-1-cyclohexanecarboxylic acid (methyl ester as internal standard) BF_3/CH_3OH complex Formic (methanoic) acid
Solvents	Dichloromethane (DCM) N-Hexane (HPLC grade) Diethyl ether (Distol) Petroleum ether Distilled water
Other apparatus	Small spatula Sonicator Rotary evaporator Hot/cold water bath GC, GC-MS
Personal protection equipment (PPE)	Hand gloves Eye goggles Disposable nose masks
Sample weight	Degraded oil (150mg) Undegraded oil (400mg) Rock extract (not known)

Appendix I-c

HPLC Column Kit

Blank column Kit for HPLC with dimensions: 10.0 mm I.D. × 1/2″ O.D. × 25 cm L (Supelco#58217). The kit includes a precision-bore polished 316 stainless steel column blank, two zero dead volume external reducing unions (internal unions, 10 mm I.D.) with nuts and ferrules for 1/16″ O.D. tubing and two 2-µm frits.

A photo of the simulated migration experiment showing steel column HPLC set-up



Appendix II-a

Peak identification for Steranes and Diasteranes

Peak sign	Peak name	Carbon number
d1	13β(H), 17α(H)- diasterane (20S)	C_{27}
d2	13β(H), 17α(H)- diasterane (20R)	C_{27}
S1	5α,14α,17α(H) cholestane (20S)	C_{27}
S2	5α,14β,17β(H) cholestane (20S)	C_{27}
S3	5α,14β,17β(H) cholestane (20R)	C_{27}
S4	5α,14α,17α(H) cholestane (20R)	C_{27}
d3a	13β(H), 17α(H)- diasterane (24S)	C_{28}
d3b	13β(H), 17α(H)- diasterane (24R)	C_{28}
d4a	13β(H), 17α(H)- diasterane (24S)	C_{28}
d4b	13β(H), 17α(H)- diasterane (24R)	C_{28}
S5	24-methyl-5α,14α,17α(H) cholestane (20S)	C_{28}
S6	24-methyl-5α,14β,17β(H) cholestane (20S)	C_{28}
S7	24-methyl-5α, 14β,17β(H)cholestane (20R)	C_{28}
S8	24-methyl-5α,14α,17α(H) cholestane (20R)	C_{28}
d5	13β(H), 17α(H)- diasterane (20S)	C_{29}
d6	13β(H), 17α(H)- diasterane (20R)	C_{29}
S9	24-ethyl-5α,14α,17α(H) cholestane (20S)	C_{29}
S10	24-ethyl-5α,14β,17β(H) cholestane (20S)	C_{29}
S11	24-ethyl-5α,14β,17β(H) cholestane (20R)	C_{29}
S12	24-ethyl-5α,14α,17α(H) cholestane (20R)	C_{29}

Appendix II-b

Peak identification for Terpanes

Peak sign	Peak name	Carbon number
Ts	18α(H)-22,29,30-trisnorneohopane	(C_{27})
Tm	17α(H)-22,29,30-trisnorneohopane	(C_{27})
28nH	17α(H)-28,30-bisnorhopane (BNH)	(C_{28})
29nH	25-nor-17α(H)-hopane (10-Desmethyl-)	(C_{29})
29H	17α(H), 21β(H)-30-norhopane	(C_{29})
29Ts	18α(H)-30-norneohopane	(C_{29})
D30	17α(H)-diahopane	(C_{30}*)
*H21'ene	Hop-17(21)-ene	(C_{30})
29M	17β(H), 21α(H)-30-normoretane	(C_{29})
OL	18α(H)+ 18β(H)-oleananes	(C_{30})
30H	17α(H), 21β(H)-hopane	(C_{30})
30H'ene	Hop-13(18)-ene	(C_{30})
30M	17β(H) 21α(H)-moretane	(C_{30})
31S	17α(H), 21β(H)-homohopane (22S)	(C_{31})
31R	17α(H), 21β(H)-homohopane (22R)	(C_{31})
Gam	Gammacerane	(C_{30})
31M	17β(H), 21α(H)-homomoretane (22S+22R)	(C_{31})
32S	17α(H), 21β(H)-bishomohopane (22S)	(C_{32})
32R	17α(H), 21β(H)-bishomohopane (22R)	(C_{32})
32M	17β(H), 21β(H)-bishomomoretane (22S+22R)	(C_{32})
31ββ	17β(H),21β(H)-homohopane	(C_{31})
33S	17α(H), 21β(H)-trishomohopane (22S)	(C_{33})
33R	17α(H), 21β(H)-trishomohopane (22R)	(C_{33})
32ββ	17β(H),21β(H)-bishomohopane	(C_{32})
34S	17α(H), 21β(H)-tetrakishomohopane (22S)	(C_{34})
34R	17α(H), 21β(H)-tetrakishomohopane (22R)	(C_{34})
35S	17α(H), 21β(H)-pentakishomohopane (22S)	(C_{35})
35R	17α(H), 21β(H)-pentakishomohopane (22R)	(C_{35})

Appendix II-c

Peak identification for Hopenes

Peak sign	Peak name	Carbon number
30	Hop-13(18)-ene	C_{30}
31S	Homohop-17(21)-ene (22S)	C_{31}
31R	Homohop-17(21)-ene (22R)	C_{31}
32S	Bishomohop-17(21)-ene (22S)	C_{32}
32R	Bishomohop-17(21)-ene (22R)	C_{32}
33S	Trishomohop-17(21)-ene (22S)	C_{33}
33R	Trishomohop-17(21)-ene (22R)	C_{33}
34S	Tetrakishomohop-17(21)-ene (22S)	C_{34}
34R	Tetrakishomohop-17(21)-ene (22R)	C_{34}
35S	Pentakishomohop-17(21)-ene (22S)	C_{35}
35R	Pentakishomohop-17(21)-ene (22R)	C_{35}

Appendix II-d

Peak identification for Diasterenes

Peak sign	Peak name	Carbon number
27βS	10β(H)-diacholest-13(17)-ene (20S)	C_{27}
27αS	10α(H)-diacholest-13(17)-ene (20S)	C_{27}
27βR	10β(H)-diacholest-13(17)-ene (20R)	C_{27}
27αR	10α(H)-diacholest-13(17)-ene (20R)	C_{27}
28αS	24-methyl-10α(H)-diacholest-13(17)-ene (20S)	C_{28}
28αR	24-methyl-10α(H)-diacholest-13(17)-ene (20R)	C_{28}
29αS	24-ethyl-10α(diacholest-13(17)-ene (20S)	C_{29}
29βR	24-ethyl-10β(diacholest-13(17)-ene (20R)	C_{29}
29αR	24-ethyl-10α(diacholest-13(17)-ene (20R)	C_{29}

Appendix II-e

Peak identification for Methyl-diasterenes

Peak sign	Peak name	Carbon number
28S	4β-methyl-10α-diaster-13,17-ene (20S)	C_{28}
28R	4β-methyl-10α-diaster-13,17-ene (20R)	C_{28}
29S	4β-methyl-10α-C28-diaster-13,17-ene (20S)	C_{29}
29R+30S	4β-methyl-10α-C28-(20R) + -C29-(20S)-diaster-13,17-ene (co-eluting)	C_{29}, C_{30}
?30x	Unknown methyldiasterene-I	C_{30}
30R	4β-methyl-10α-C29-diaster-13,17-ene (20R)	C_{30}
?30y	Unknown methyldiasterene-II	C_{30}

Appendix II-f

Peak identification for (C_{30}-C_{33}) hopanoic acids

Peak	Peak name
1	C_{30}- 17α(H), 21β(H)-hopanoic acid (22S)
2	C_{30}-17α(H), 21β(H)-hopanoic acid (22R)
3	C_{30}-17β(H), 21α(H)-hopanoic acid (22S)
4	C_{30}-17β(H), 21α(H)-hopanoic acid (22R)
5	C_{30}-17β(H), 21β(H)-hopanoic acid (22S)
6	C_{30}-17β(H), 21β(H)-hopanoic acid (22R)
7	C_{31}-17α(H), 21β(H)-hopanoic acid (22S)
8	C_{31}-17α(H), 21β(H)-hopanoic acid (22R)
9	C_{31}-17β(H), 21α(H)-hopanoic acid (22S)
10	C_{31}-17β(H), 21α(H)-hopanoic acid (22R)
11	C_{31}-17β(H), 21β(H)-hopanoic acid (22S)
12	C_{31}-17β(H), 21β(H)-hopanoic acid (22R)
13	C_{32}-17α(H), 21β(H)-hopanoic acid (22S)
14	C_{32}-17α(H), 21β(H)-hopanoic acid (22R)
15	C_{32}-17β(H), 21α(H)-hopanoic acid (22S)
16	C_{32}-17β(H), 21α(H)-hopanoic acid (22R)
17	C_{32}-17β(H), 21β(H)-hopanoic acid (22S)
18	C_{32}-17β(H), 21β(H)-hopanoic acid (22R)
19	C_{33}-17α(H), 21β(H)-hopanoic acid (22S)
20	C_{33}-17α(H), 21β(H)-hopanoic acid (22R)
21	C_{33}-17β(H), 21α(H)-hopanoic acid (22S)
22	C_{33}-17β(H), 21α(H)-hopanoic acid (22R)
23	C_{33}-17β(H), 21β(H)-hopanoic acid (22S)
24	C_{33}-17β(H), 21β(H)-hopanoic acid (22R)

Appendix II-g

Peak identification for Aromatic hydrocarbon compounds

Peak	Peak name
N	Naphthalene
2-MN, 1-MN	Methylnaphthalene
2-EN, 1-EN	Ethylnaphthalenes
2,6+2,7- DMN 1,3+1,7- DMN 1,6- DMN 1,4+2,3- DMN 1,5- DMN 1,2-DMN	Dimethylnaphthalenes
1,3,7- TMN 1,3,6- TMN 1,4,6+1,3,5- TMN 2,3,6- TMN 1,2,7+1,6,7+1,2,6- TMN 1,2,4- TMN 1,2,5- TMN 1,2,3- TMN	Trimethynaphthalenes
P	Phenanthrene
3-MP 2-MP 9-MP 1-MP	Methylphenantrenes
3,6-DMP+(2+3+1EP) 2,6-+ 3,5- DMP 2,7- DMP 3,10+1,3+2,10+3,9- DMP 1,6+2,5+2,9- DMP 1,7- DMP 2,3- DMP 1,9+4,9+4,10- DMP 1,8- DMP DMP?? (Unknown isomer)	Dimethylphenanthrenes (+ethylphenanthrenes)
DBT	Dibenzothiophene
4-MDBT 3-,+2-MDBT 1-MDBT	Methyldibenzothiophenes
4-EDBT	Ethyldibenzothiophene
?4,6-DMDBT 2,4+2,6-DMDBT 1,4-DMDBT 1,3-DMDBT	Dimethyldibenzothiophenes
Biphenyl	Biphenyl
2-MB 3-MB 4-MB	Methylbiphenyls
DPM	Diphenylmethane
DBF	Dibenzofuran
Fluorene	Fluorene
3-MF 2-MF 1-MF 4-MF	Methylfluorenes

Appendix III-a: Field Samples Olefin and Acid Data (On CD)

List on CD ROM

Hopanoic Acid Data

n-Acid Data

n-Alkene Data

Triterpene Data

Diasterene Data

Appendix III-b: Field Samples Regular Biomarker Data (On CD)

List on CD ROM

n-Alkane and Isoprenoid Alkane Data

Triterpane Data

Sterane and Diasterane Data

Aromatic Hydrocarbon Data

Aromatic Hydrocarbon Data (Cont'd)

Aromatic Steroid Hydrocarbon Data

Biomarker Parameter Data I

Biomarker Parameter Data II

Biomarker Parameter Data III

GC Peak Areas (n-alkanes)

GC-MS Peak Areas (Steranes)

GC-MS Peak Areas (Terpanes)

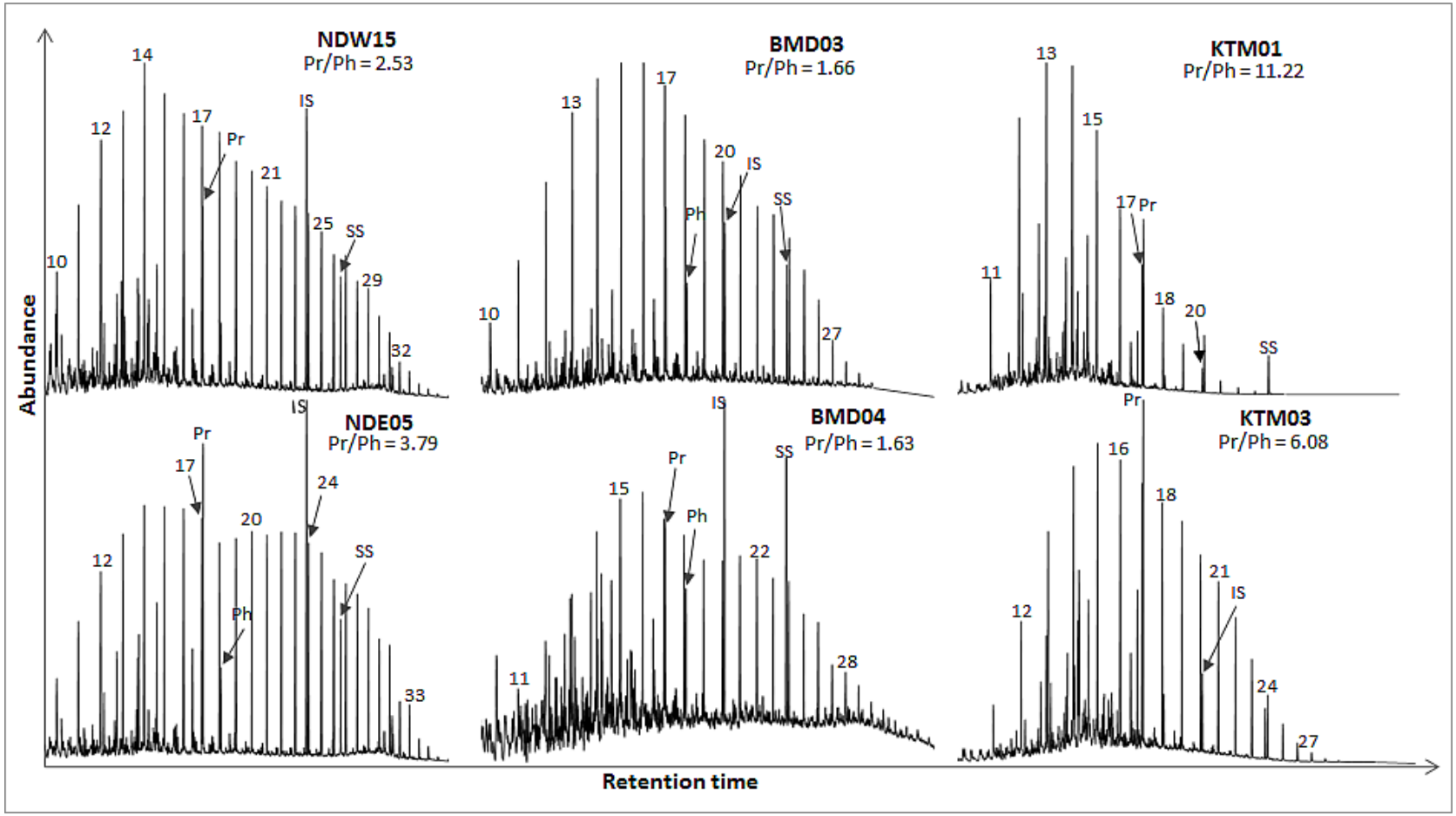
GC-MS Peak Areas (Aromatics)

GC-MS Peak Areas (Aromatics Cont'd)

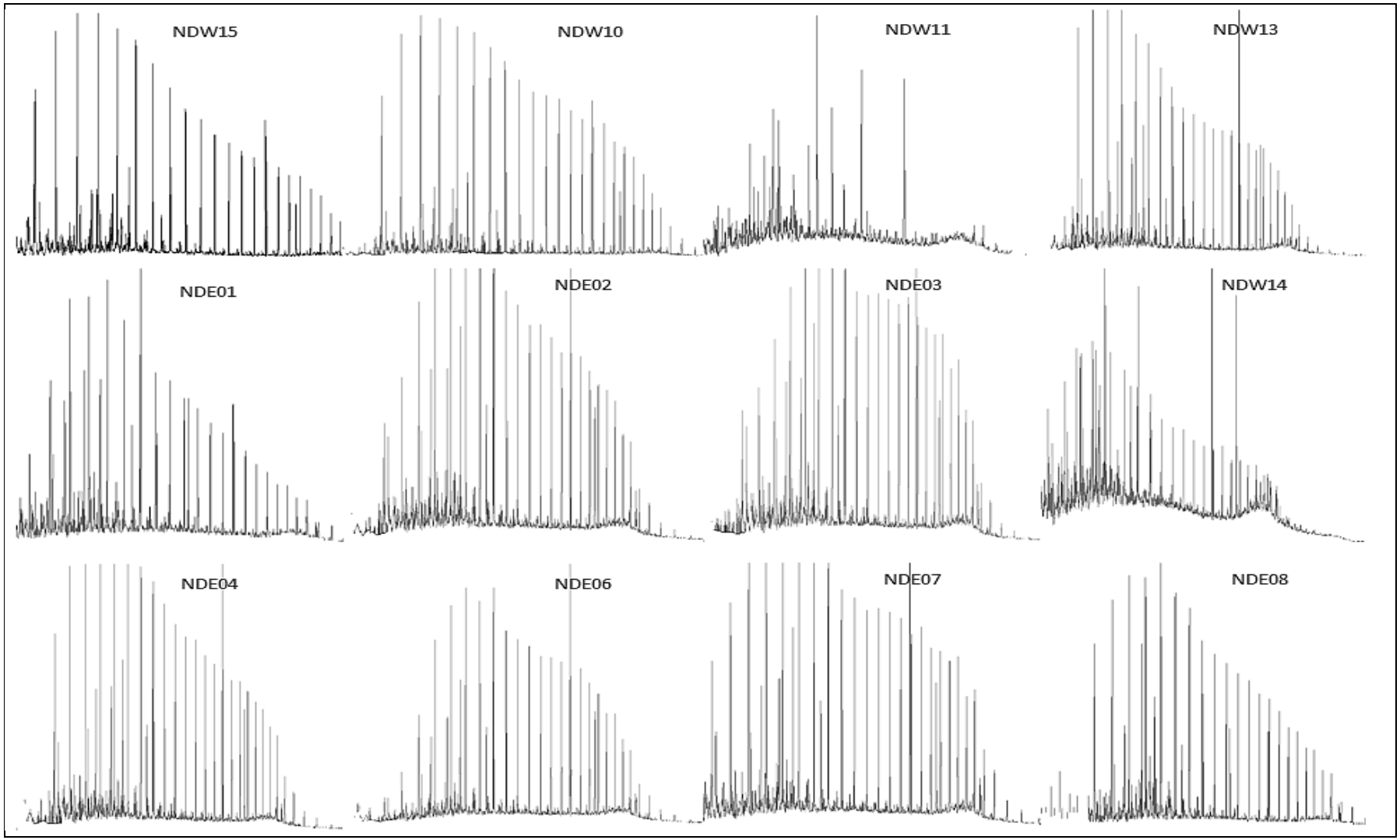
GC-MS Peak Areas (MAS/TAS HCs)

Appendix III-c

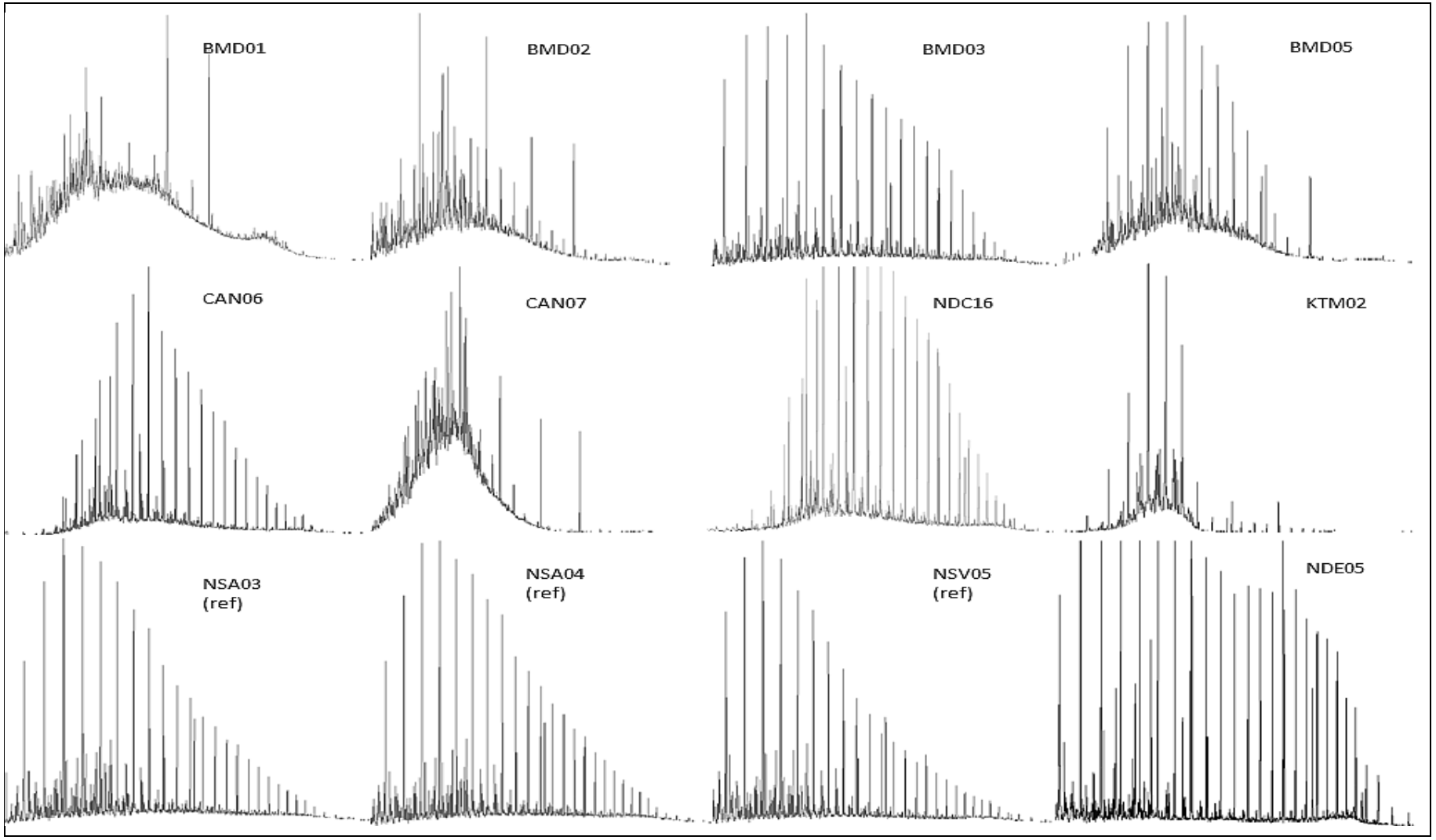
Gas chromatogram fingerprints of most case study oils (and some reference oils) showing the distribution of n-alkanes.



IIIc: GC fingerprints cont’d

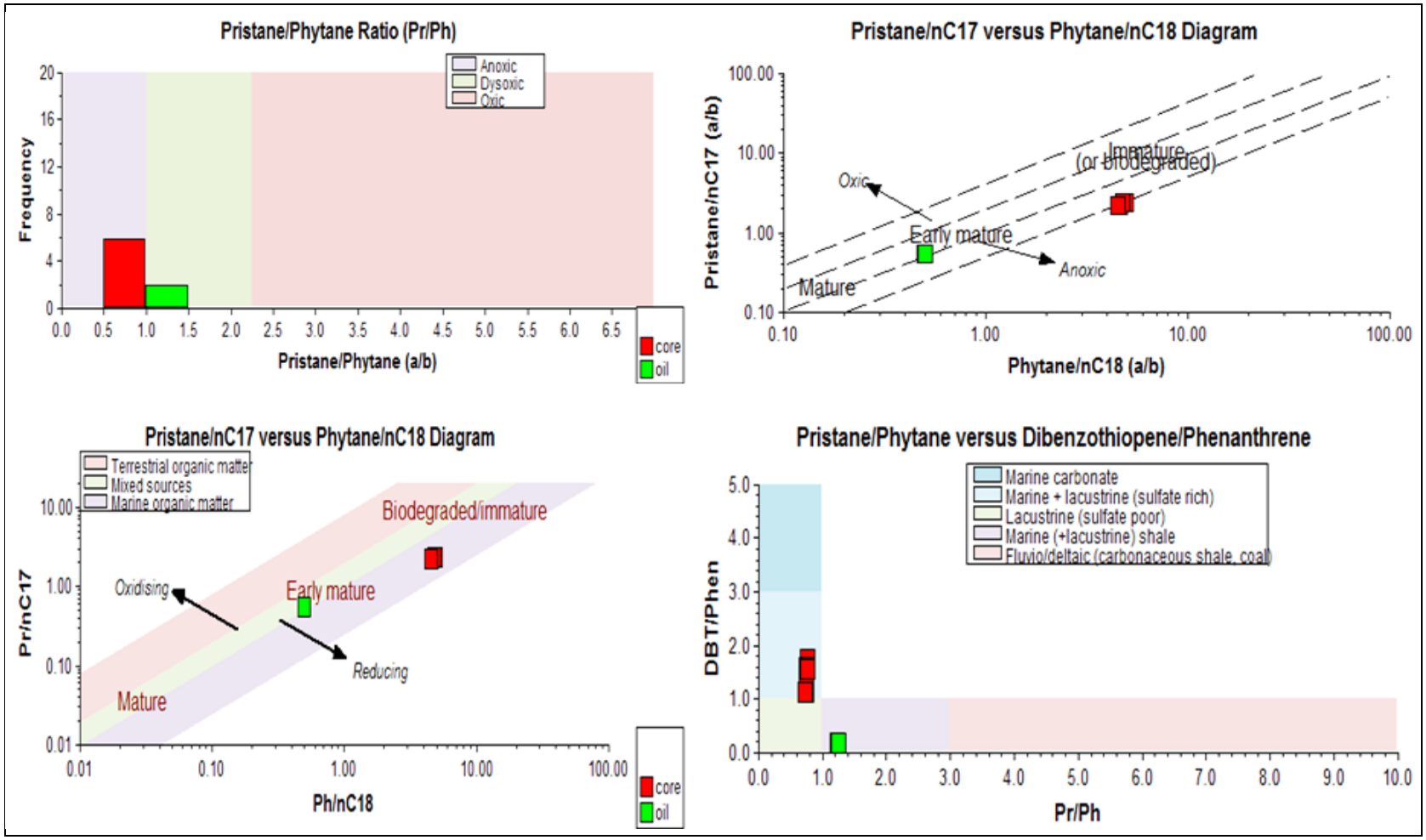


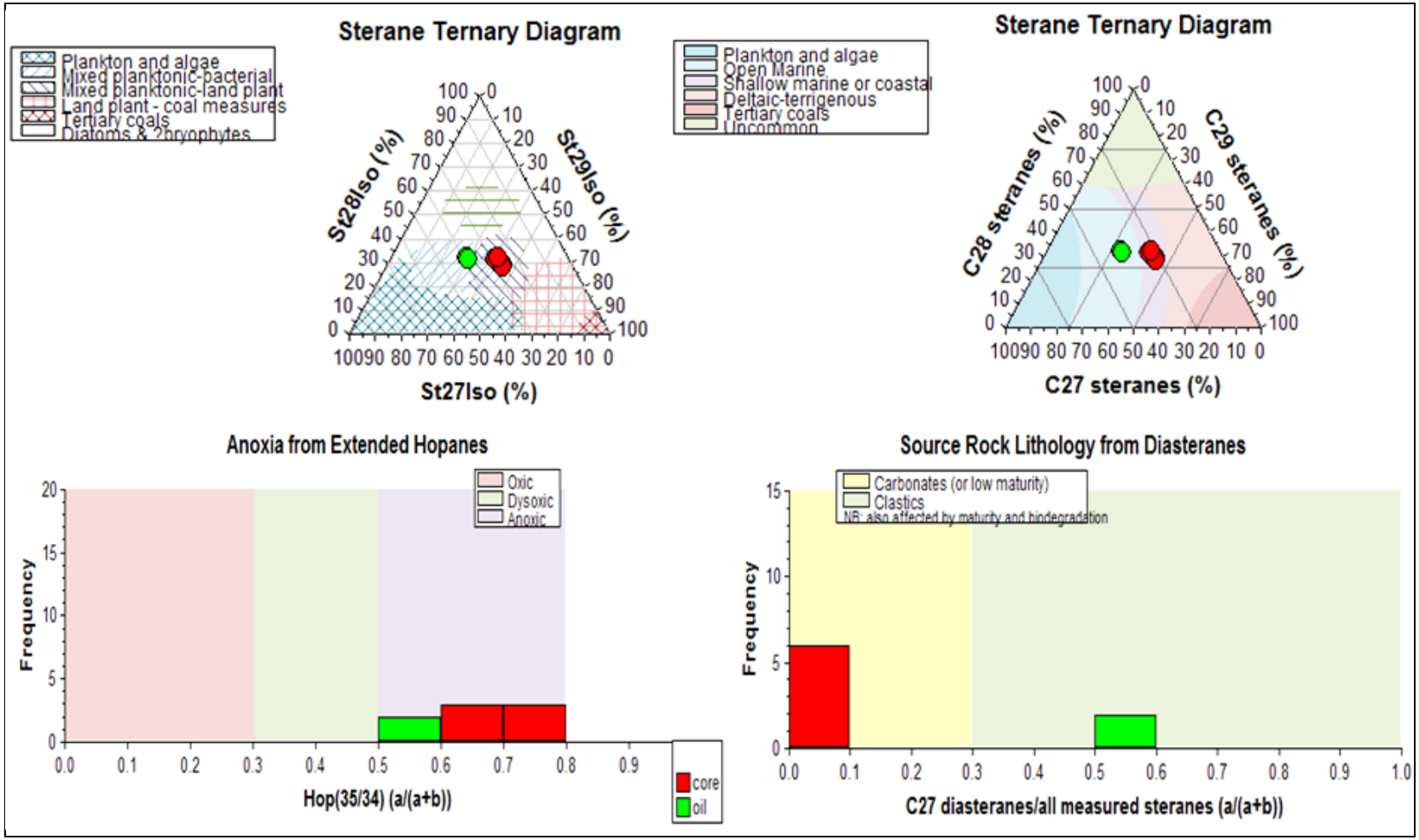
IIIc: GC fingerprints cont’d



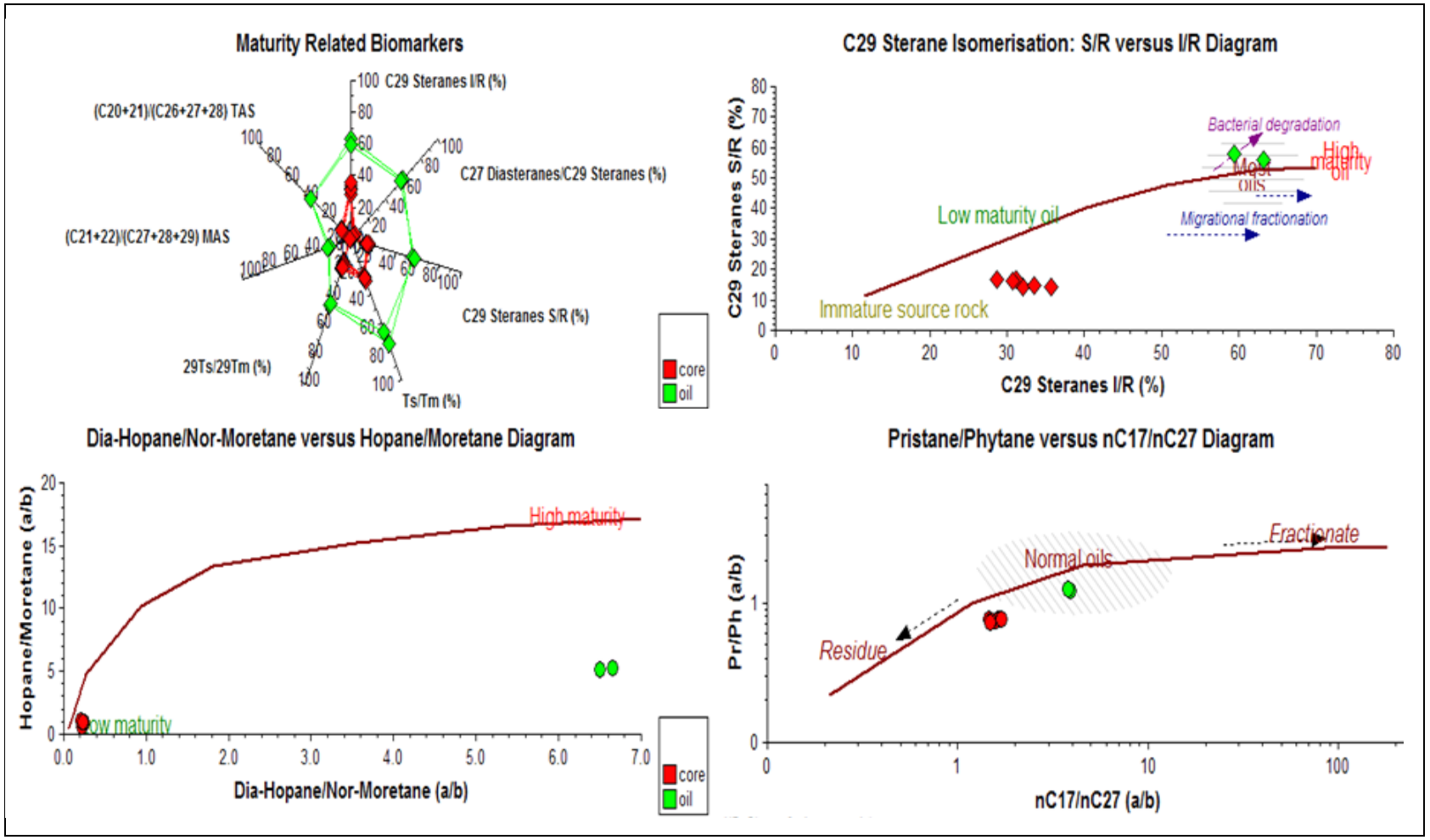
Appendix III-d

Test for Kerogen type using various biomarker relationships

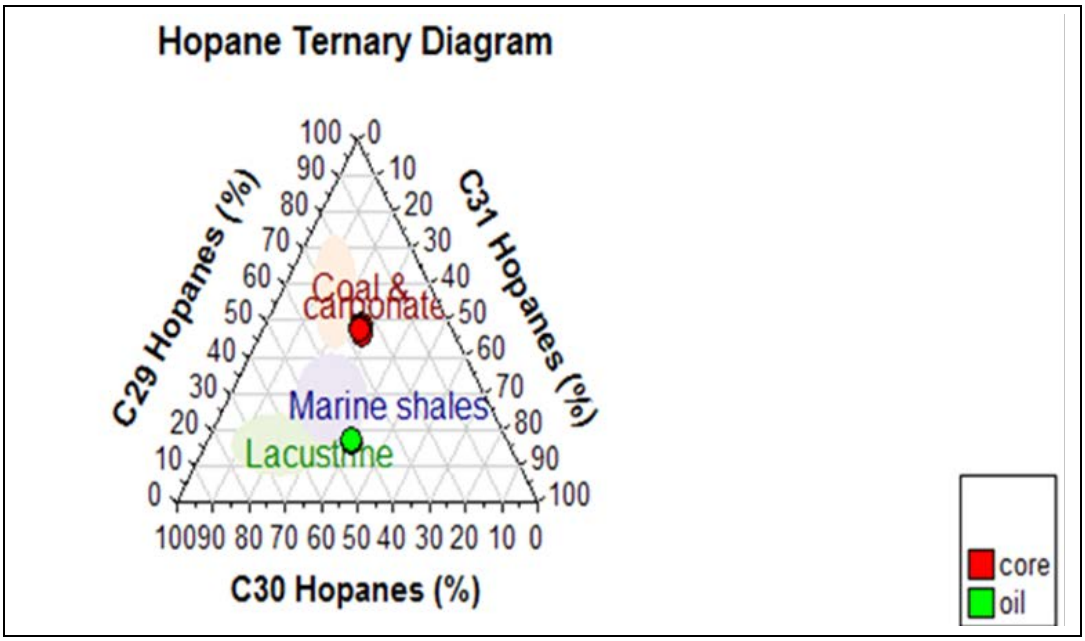



Sterane Ternary Diagram
Plankton and algae
Mixed planktonic-bacterial
Mixed planktonic-land plant
Land plant - coal measures
Tertiary coals
Diatoms & ?bryophytes
St28Iso (%)
St29Iso (%)
St27Iso (%)
Sterane Ternary Diagram
Plankton and algae
Open Marine
Shallow marine or coastal
Deltaic-terrigenous
Tertiary coals
Uncommon
C28 steranes (%)
C29 steranes (%)
C27 steranes (%)
Anoxia from Extended Hopanes
Oxic
Dysoxic
Anoxic
Frequency
Hop(35/34) (a/(a+b))
core
oil
Source Rock Lithology from Diasteranes
Carbonates (or low maturity)
Clastics
NB: also affected by maturity and biodegradation
Frequency
C27 diasteranes/all measured steranes (a/(a+b))

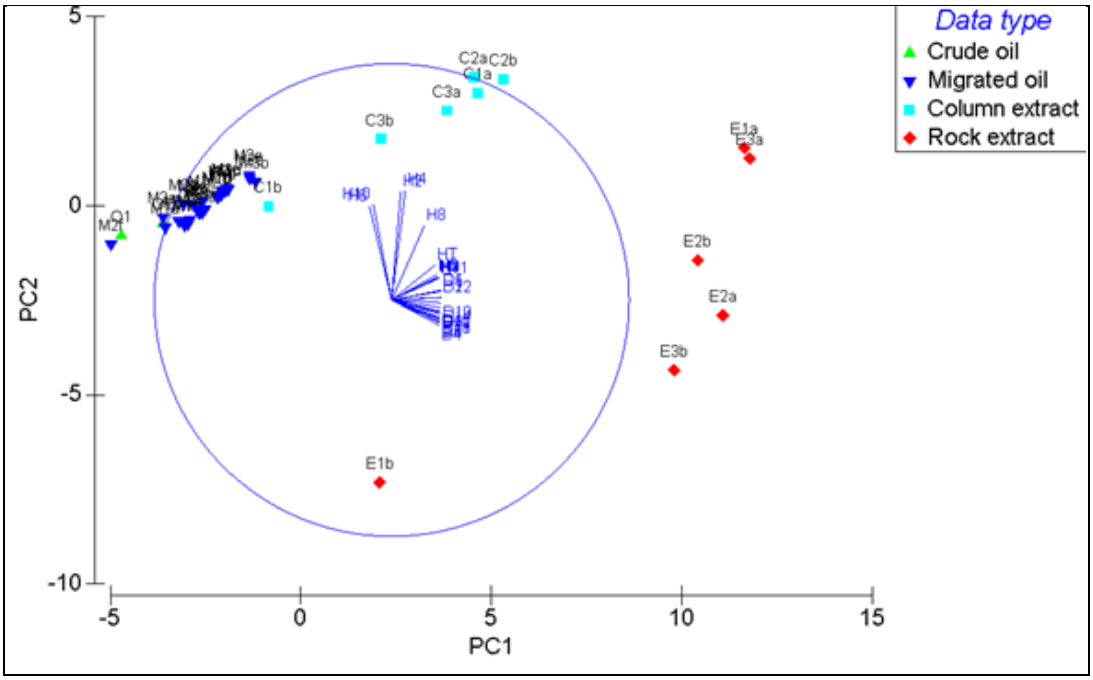
IIIc: Test for maturity of migration core and oil samples using various biomarker relationships



IIIc: Inference of the clay and the oil source rock lithologies using tri-plot of the C_{29}-C_{31} hopanes.



PCA merged (scores and loading) plots of olefins (only) variables in the migration samples.



Appendix IV-a: Migration Study Olefin and Acid Data (On CD)

List on CD ROM

Olefin Data

Olefin Data Cont'd

Total n-acid (Corrected) Data

n-Acid Data (Estimated)

Hopanoic Acid Data

Appendix IV-b: Migration Study Biomarker Data and PCA Data Sets (On CD)

List on CD ROM

n-Alkane (GC Peak Areas)

Steranes (GC-MS Peak Areas)

Terpanes (GC-MS Peak Areas)

Aromatic HCs (GC-MS Peak Areas)

Aromatic HCs (GC-MS Peak Areas) cont'd

Aromatic Steroid HCs (GC-MS Peak Areas)

Saturate HC Data for PCA

Saturate HC Data for PCA cont'd

Saturate HC Data for PCA cont'd

Aromatic HC Data for PCA

Aromatic HC Data for PCA cont'd

IV-b: Olefin Data for PCA

				Hopenes (H)												Diacholest-13(17)-ene (D)														
			Variables-->	Hop-13(18)-	Homohop-17(21)-	Homohop-17(21)-	Bishomohop-	Bishomohop-	Trishomohop-	Trishomohop-	Tetrakisomohop-	Tetrakisomohop-	Pentakishomoho	Pentakishomoho	Tot Hopenes	(20S)-10β(H)-	(20S)-10α(H)-	(20R)-10β(H)-	(20R)-10α(H)-	(20S)-24-methyl-	(20R)-24-methyl-	(20S)-24-ethyl-	(20R)-24-ethyl-	(20R)-24-ethyl-	(20S)-4β-methyl-	(20R)-4β-methyl-	(20S)-4β-methyl-	4β-methyl-	?4β-methyl-	(20R)-4β-methyl-	?4β-methyl-	Tot. Diastere
Sample ID	PC objects	DataType	Particle size	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	HT	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13	D14	D15	D16	DT
NS-1	O1	Crude oil	n/a	2	14	5	11	5	9	3	7	3	5	2	65	70	330	35	174	312	102	489	36	238	53	33	67	55	17	50	21	2082
NS-2	O2	Crude oil	n/a	3	17	7	15	11	11	8	8	5	8	4	98	99	466	60	391	444	172	852	85	437	77	71	103	119	36	73	42	3527
1-4b	M1a	migrated oil	4mm-1mm	6	16	10	13	15	9	9	7	8	7	4	103	87	409	55	381	394	155	797	52	428	78	79	90	129	34	85	51	3304
1-4c	M1b	migrated oil	4mm-1mm	7	17	10	13	16	13	12	9	7	8	6	118	97	459	78	467	450	185	922	99	503	92	92	107	167	46	95	56	3915
1-4d	M1c	migrated oil	4mm-1mm	12	28	17	20	26	19	18	12	9	10	6	177	146	672	116	674	628	239	1268	92	668	117	118	137	212	63	110	72	5329
1-4e	M1d	migrated oil	4mm-1mm	15	30	19	20	24	19	16	13	11	13	10	190	167	791	136	830	752	294	1564	136	830	152	157	176	268	82	139	92	6564
1-4g	M1e	migrated oil	4mm-1mm	26	29	21	27	31	22	20	16	12	14	13	230	177	828	150	872	802	349	1647	131	890	164	163	188	277	84	132	92	6947
63-1a	M2a	migrated oil	1mm-63um	3	17	10	17	14	13	9	10	5	8	3	108	79	340	46	249	333	129	633	73	345	121	96	105	189	48	205	47	3040
63-1c	M2b	migrated oil	1mm-63um	12	30	18	21	25	20	15	13	10	13	10	188	169	800	132	785	754	292	1572	96	838	184	182	182	278	77	188	101	6630
63-1e-ov	M2c	migrated oil	1mm-63um	17	32	22	25	23	20	17	18	13	14	8	209	180	820	144	813	788	336	1607	158	865	167	165	189	281	80	153	95	6842
63-1f	M2d	migrated oil	1mm-63um	24	30	23	24	26	23	18	15	10	16	11	219	191	886	154	922	856	349	1763	136	939	179	180	211	309	104	164	104	7447
63-1g	M2e	migrated oil	1mm-63um	25	39	26	34	37	27	26	22	18	18	16	288	229	1103	205	1231	1063	461	2259	139	1229	225	234	257	510	185	132	110	9464
63a	M3a	migrated oil	<63um	8	23	13	19	20	17	12	10	9	11	6	148	136	631	103	608	612	254	1261	141	709	176	176	166	273	78	256	95	5674
63b	M3b	migrated oil	<63um	23	39	26	33	31	26	23	19	16	17	13	265	249	1119	204	1158	1068	501	2288	228	1312	358	374	296	516	152	444	189	10454
63e	M3c	migrated oil	<63um	20	40	24	32	33	27	24	23	16	16	14	269	230	1066	185	1026	1013	440	2095	162	1174	323	327	283	466	124	364	159	9435
63f	M3d	migrated oil	<63um	18	31	20	24	26	24	19	18	13	13	10	216	184	833	129	740	789	334	1570	131	830	257	228	222	329	88	279	110	7054
63g-ov	M3e	migrated oil	<63um	10	20	11	18	15	16	14	13	9	12	9	146	124	561	77	462	546	224	1032	101	544	146	123	133	199	57	166	65	4560
1-4a2	M1f	migrated oil	4mm-1mm	7	18	10	15	15	11	10	7	7	7	6	112	122	580	96	566	542	215	1100	67	580	117	107	117	163	44	100	67	4582
1-4b2	M1g	migrated oil	4mm-1mm	10	19	11	12	16	12	9	8	7	8	6	119	122	578	91	531	551	203	1099	85	575	115	110	138	197	65	109	65	4633
1-4c2	M1h	migrated oil	4mm-1mm	14	29	18	21	24	18	17	14	9	13	9	186	175	822	138	808	786	251	1573	128	823	161	158	189	294	89	146	95	6638
1-4d2	M1i	migrated oil	4mm-1mm	24	31	21	25	21	22	17	13	8	12	9	202	198	882	155	923	844	361	1696	183	911	167	142	190	160	89	132	94	7125
1-4g2ov	M1j	migrated oil	4mm-1mm	16	29	20	23	24	23	18	16	16	14	11	209	195	909	141	887	833	311	1663	132	837	178	177	198	305	88	141	91	7086
63-1f2	M2f	migrated oil	1mm-63um	0	9	3	9	6	8	4	6	2	6	2	54	65	278	23	173	257	85	404	42	237	49	30	58	58	16	58	21	1854
63-1g2ov	M2g	migrated oil	1mm-63um	3	22	12	16	15	16	13	15	10	12	6	140	118	534	69	415	521	200	917	120	503	108	97	120	163	55	100	46	4085
63a2	M3f	migrated oil	<63um	6	20	11	15	14	13	11	10	5	8	4	117	116	507	77	422	485	193	911	115	533	163	150	139	247	69	240	76	4445
63b2	M3g	migrated oil	<63um	10	23	12	17	17	15	11	11	6	10	6	138	149	659	110	558	626	263	1223	129	649	180	164	167	256	80	226	78	5517
63d2	M3h	migrated oil	<63um	8	23	13	17	17	14	10	11	6	10	6	136	148	653	96	546	623	213	1191	132	637	170	157	159	249	73	194	79	5319
63f2	M3i	migrated oil	<63um	5	19	11	15	15	15	9	9	6	9	5	118	127	588	83	470	569	227	1084	155	567	164	132	143	212	60	206	69	4857
63g2-ov	M3j	migrated oil	<63um	7	21	13	17	15	15	11	13	7	11	8	138	146	635	95	519	597	232	1112	112	565	154	135	146	220	70	163	73	4977
1-4col	C1a	col.extract	4mm-1mm	1181	365	339	153	162	133	121	111	102	111	95	2872	3572	12702	3559	14319	11089	8076	31876	4585	23247	19261	21020	7866	21059	4439	24101	7579	218349
63-1col	C2a	col.extract	1mm-63um	932	441	410	185	213	161	153	144	128	140	130	3037	2962	10474	2967	11941	9378	6972	27539	5169	20275	16399	18268	6759	17859	3320	21190	6727	188198
63col	C3a	col.extract	<63um	690	250	232	118	116	98	88	84	69	80	73	1897	2331	8144	2202	9143	7331	5460	21347	5788	15768	12051	13674	5292	12478	2676	17343	5282	146310
1-4col2	C1b	col.extract	4mm-1mm	11	47	16	28	12	20	8	14	6	13	4	179	395	1186	187	650	1072	742	2529	634	1566	1643	947	750	1948	463	3467	498	18675
63-1col2	C2b	col.extract	1mm-63um	1368	520	476	199	211	172	158	144	124	135	113	3621	5183	17411	4875	19346	15465	11556	44323	7584	32404	27001	29118	11330	29177	6639	35374	11003	307789
63col2	C3b	col.extract	<63um	242	130	104	73	64	60	50	48	39	44	34	886	993	3568	815	3729	3257	2262	8931	2300	6133	4757	4990	2195	5293	1210	7013	1969	59415
KC-14a	E1a	rock extract	4mm-1mm	49827	2617	12452	578	3747	0	2945	548	1882	0	2207	76802	54177	203545	55314	245721	149725	103654	482465	120402	373346	348149	404874	119535	298905	78627	498821	167469	6020032
KC-163a	E2a	rock extract	1mm-63um	44059	0	10623	0	3484	0	2750	464	2017	0	2121	65518	53406	214624	56030	254545	162904	97299	473743	135374	347162	353689	414573	119358	257070	53159	430741	142081	5839043
KC-63a	E3a	rock extract	<63um	54264	1779	12553	341	3890	0	3241	556	2111	0	2638	81372	57235	211071	59314	251507	188349	138088	557532	153425	386969	394131	451020	134572	291675	64045	481104	155649	6528886
KC-14b	E1b	rock extract	4mm-1mm	0	0	0	0	0	0	0	0	0	0	0	0	392	2441	44135	230196	993	27214	192292	70318	320752	9389	383604	1357	134057	9146	67069	115453	2818291
KC-163b	E2b	rock extract	1mm-63um	39130	0	8985	101	2540	0	2182	248	1473	0	1317	55975	18174	110725	50765	228732	81398	43308	261759	118628	309959	221689	370399	79205	182504	29327	374237	123433	4249599
KC-63b	E3b	rock extract	<63um	42004	0	9600	0	2724	0	2229	0	1361	0	1437	59354	15840	106363	53221	243688	83855	61723	280774	135767	340502	232633	400824	84112	201168	31529	426115	136030	4615090

IV-b: Selected Biomarker Parameter Data for PCA

Biomarker Parameters (P)																												
		Pr/Ph	Pr/nC17	Ph/nC18	nC17/nC27	CPI-1	DiaSt (%)	St29S/R	St29I/R	%27St	%29St	%St27Iso	%St28Iso	%St29Iso	C29/C27	St29/Tt30	Ts/Tm	Hop/Mor	Dia/NorM	29Ts/29Tm	%22S (C31)	Gam-I	HHI	Hop(35/34)	MPI(1)	MPR	Phen/nC18	DBT/PHEN	TAS/MAS
Sample ID	PC objects	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P18	P19	P20	P21	P22	P23	P24	P25	P26	P27	P28
NS-1	O1	1.23	0.55	0.50	3.89	0.90	59.6	1.28	1.72	43.1	25.1	38.8	32.4	28.8	0.70	12.79	2.94	5.18	6.50	0.83	56.5	0.14	2.10	1.03	0.65	0.92	0.09	0.18	4.70
NS-2	O2	1.24	0.54	0.50	3.81	0.91	57.8	1.39	1.47	42.4	25.6	38.7	32.0	29.3	0.71	16.74	1.92	5.28	6.66	0.81	56.2	0.13	1.84	1.04	0.63	0.97	0.10	0.17	6.33
1-4b	M1a	1.26	0.56	0.50	4.05	0.86	56.9	1.03	1.28	32.7	31.6	40.2	31.4	28.4	0.97	13.94	2.54	5.14	5.62	0.86	56.5	0.14	2.10	1.02	0.63	1.08	0.10	0.03	2.26
1-4c	M1b	1.23	0.55	0.50	3.96	0.87	54.4	1.14	1.49	34.8	31.5	38.6	31.6	29.9	0.90	14.88	2.00	4.92	4.22	0.83	56.1	0.15	2.10	1.04	0.65	0.93	0.10	0.06	2.14
1-4d	M1c	1.24	0.55	0.50	3.98	0.88	54.1	0.96	1.36	34.2	35.3	39.0	31.2	29.8	1.03	14.55	2.86	4.83	5.53	0.84	56.2	0.15	2.28	1.09	0.65	0.94	0.10	0.03	1.55
1-4e	M1d	1.24	0.55	0.50	3.88	0.88	53.6	1.18	1.51	35.9	31.3	38.5	31.5	30.0	0.87	14.77	1.86	4.79	5.50	0.80	56.0	0.15	2.09	1.03	0.63	1.01	0.10	0.17	2.64
1-4g	M1e	1.23	0.55	0.50	3.88	0.87	53.0	1.26	1.60	35.7	30.0	37.4	29.5	33.1	0.84	14.69	3.04	4.80	4.01	0.84	55.7	0.15	2.28	1.04	0.62	1.04	0.09	0.09	1.87
63-1a	M2a	1.17	0.55	0.52	3.82	0.91	49.4	1.51	0.84	30.8	35.9	37.4	29.7	32.8	1.17	15.18	2.22	4.80	4.99	0.81	56.1	0.15	2.18	1.02	0.64	0.92	0.08	0.17	1.22
63-1c	M2b	1.30	0.54	0.48	4.18	0.86	52.6	1.27	1.56	37.3	29.9	36.4	29.8	33.9	0.80	15.81	3.01	5.90	6.34	0.80	55.8	0.11	2.05	1.13	0.66	0.93	0.11	0.19	2.95
63-1e-ov	M2c	1.24	0.55	0.50	4.16	0.85	55.4	1.11	1.28	36.5	32.1	32.4	33.4	34.2	0.88	13.44	1.93	4.82	5.02	0.80	55.7	0.14	2.13	0.99	0.63	1.02	0.10	0.18	3.58
63-1f	M2d	1.23	0.54	0.49	3.70	0.89	53.9	1.15	1.50	37.8	30.7	37.6	31.6	30.9	0.81	13.98	1.96	5.13	4.99	0.79	55.9	0.14	2.02	1.14	0.66	1.02	0.11	0.18	4.56
63-1g	M2e	1.23	0.54	0.49	3.93	0.89	56.0	1.04	1.24	35.6	33.0	38.5	31.3	30.2	0.93	13.54	1.89	4.85	4.08	0.83	56.1	0.15	2.16	1.00	0.64	0.93	0.12	0.18	2.47
63a	M3a	1.30	0.54	0.48	3.99	0.88	55.5	1.55	1.32	38.2	29.0	39.6	31.4	29.0	0.76	16.11	3.03	5.35	5.70	0.83	56.1	0.13	2.01	1.04	0.63	0.96	0.10	0.05	1.88
63b	M3b	1.24	0.54	0.49	3.47	0.93	56.0	0.93	1.51	35.5	33.0	37.5	32.0	30.6	0.93	15.64	2.01	5.18	4.66	0.82	56.5	0.14	2.02	1.01	0.65	0.91	0.09	0.09	1.16
63e	M3c	1.34	0.54	0.47	3.54	0.91	56.1	0.98	1.21	33.9	33.5	38.8	31.9	29.3	0.99	14.25	3.17	5.15	6.17	0.85	55.9	0.14	2.19	1.01	0.63	1.01	0.10	0.05	1.44
63f	M3d	1.33	0.54	0.47	3.83	0.91	54.3	0.97	1.41	35.7	33.2	39.2	32.1	28.7	0.93	15.16	2.12	5.55	5.63	0.81	56.2	0.12	1.96	1.10	0.66	0.91	0.09	0.06	1.37
63g-ov	M3e	1.26	0.54	0.48	3.87	0.88	56.1	1.35	1.63	39.5	28.2	38.7	32.0	29.3	0.71	14.81	2.08	4.91	5.68	0.80	55.8	0.15	2.17	1.04	0.66	0.91	0.10	0.06	3.61
1-4a2	M1f	1.22	0.53	0.48	3.68	0.88	53.2	0.87	1.32	32.8	38.1	37.2	29.9	33.0	1.16	66.83	1.56	3.91	4.50	0.96	56.3	0.19	2.05	1.00	0.59	0.86	0.11	0.09	2.87
1-4b2	M1g	1.24	0.54	0.48	3.75	0.87	60.6	0.84	1.23	36.6	35.1	36.4	29.9	33.8	0.96	41.20	2.94	5.85	5.43	0.81	55.6	0.11	2.11	1.16	0.65	0.93	0.10	0.11	1.88
1-4c2	M1h	1.24	0.54	0.49	3.89	0.88	54.3	1.09	1.63	36.1	30.2	39.3	31.2	29.5	0.84	24.97	1.95	4.78	4.23	0.80	56.1	0.15	2.16	0.95	0.64	0.91	0.10	0.08	1.13
1-4d2	M1i	1.21	0.54	0.50	3.84	0.89	55.2	1.23	1.67	37.0	29.3	38.5	31.3	30.2	0.79	16.17	3.06	4.93	6.24	0.81	55.7	0.15	2.34	1.01	0.64	0.92	0.10	0.06	1.18
1-4g2ov	M1j	1.26	0.55	0.49	4.00	0.88	54.7	1.16	1.41	37.4	29.5	37.4	31.3	31.3	0.79	18.46	2.87	4.81	4.88	0.79	55.2	0.16	2.30	0.98	0.64	0.92	0.11	0.18	5.62
63-1f2	M2f	1.25	0.54	0.49	3.59	0.91	54.0	1.13	1.54	36.7	30.0	40.1	31.1	28.8	0.82	21.17	2.93	4.80	5.07	0.81	55.8	0.16	2.32	0.97	0.65	1.08	0.10	0.18	3.55
63-1g2ov	M2g	1.29	0.54	0.48	3.96	0.91	55.5	1.18	1.56	36.5	28.5	37.1	30.1	32.8	0.78	41.66	3.19	5.25	5.20	0.82	56.3	0.14	2.09	1.12	0.63	1.06	0.10	0.18	0.64
63a2	M3f	1.24	0.54	0.49	4.15	0.83	55.1	1.45	1.47	39.9	27.5	39.9	31.2	28.9	0.69	184.57	1.98	5.06	4.86	0.83	56.2	0.16	1.99	1.12	0.64	1.04	0.10	0.05	0.88
63b2	M3g	1.22	0.54	0.49	4.09	0.84	54.1	1.48	1.66	38.5	26.4	38.7	31.4	29.9	0.69	63.03	2.29	4.88	4.79	0.79	55.6	0.15	2.13	1.02	0.64	1.05	0.09	0.04	1.13
63d2	M3h	1.32	0.54	0.47	4.23	0.84	55.3	1.31	1.70	38.3	27.9	38.1	31.6	30.3	0.73	78.41	3.57	4.98	7.24	0.81	56.2	0.15	2.17	1.01	0.62	1.02	0.10	0.07	0.94
63f2	M3i	1.20	0.54	0.50	4.00	0.83	56.5	1.42	1.43	38.7	26.1	39.6	31.8	28.6	0.67	74.97	1.77	4.64	4.15	0.84	55.7	0.15	2.13	1.05	0.66	0.90	0.09	0.06	0.98
63g2-ov	M3j	1.20	0.54	0.50	3.73	0.87	57.7	1.05	1.58	38.6	28.9	42.4	29.5	28.1	0.75	25.69	2.14	6.09	6.36	0.80	56.0	0.12	1.88	1.11	0.65	0.93	0.10	0.07	0.99
1-4col	C1a	1.18	0.55	0.51	4.00	0.86	52.4	1.02	1.39	38.8	30.4	37.1	31.9	31.0	0.78	14.53	2.56	4.30	3.75	0.82	55.3	0.14	2.17	1.02	0.62	1.02	0.09	0.12	0.64
63-1col	C2a	1.26	0.54	0.49	3.00	0.94	58.9	0.86	1.37	41.4	31.8	38.6	31.4	30.0	0.77	12.94	2.59	4.48	4.01	0.86	54.9	0.14	2.18	1.08	0.63	0.88	0.18	0.20	0.38
63col	C3a	1.29	0.54	0.48	3.53	0.90	56.3	1.16	1.12	41.7	29.3	38.2	30.0	31.8	0.70	15.61	3.16	4.71	5.21	0.82	55.9	0.14	2.02	1.06	0.62	0.96	0.22	0.09	0.93
1-4col2	C1b	1.24	0.54	0.49	3.96	0.91	54.1	1.13	1.53	37.2	29.8	37.5	31.6	30.8	0.80	33.30	2.05	5.49	5.01	0.72	55.3	0.11	1.88	1.10	0.63	1.05	0.13	0.18	7.49
63-1col2	C2b	1.25	0.54	0.49	3.21	0.93	52.2	0.73	1.31	35.4	36.0	37.7	31.6	30.7	1.02	34.95	1.85	4.63	4.29	0.81	54.3	0.12	1.92	1.18	0.63	0.97	0.12	0.21	0.24
63col2	C3b	1.26	0.54	0.49	3.79	0.87	54.0	1.15	1.38	36.6	31.9	39.1	31.8	29.2	0.87	47.89	3.44	4.99	3.91	0.86	55.3	0.14	2.12	1.03	0.64	0.93	0.12	0.07	0.16
KC-14a	E1a	0.75	2.38	4.81	1.45	0.88	2.4	0.20	0.40	34.0	47.6	28.2	31.4	40.4	1.23	4.80	0.35	0.80	0.24	0.19	29.1	0.95	0.56	2.12	0.50	0.61	0.38	1.26	0.00
KC-163a	E2a	0.76	2.34	4.82	1.63	0.72	3.5	0.16	0.47	32.0	48.7	28.0	31.9	40.1	1.30	4.46	0.36	0.66	0.22	0.20	29.3	0.98	0.56	2.08	0.56	0.64	0.41	1.73	0.01
KC-63a	E3a	0.74	2.22	4.63	1.59	0.98	1.9	0.17	0.51	31.9	49.2	26.9	32.6	40.5	1.30	6.48	0.44	0.92	0.22	0.27	28.1	0.96	0.56	2.24	0.57	0.67	0.49	1.13	0.01
KC-14b	E1b	0.75	2.36	4.92	1.50	1.00	3.0	0.20	0.45	31.8	49.5	26.6	29.9	43.5	1.31	4.79	0.35	1.03	0.24	0.22	28.6	0.95	0.55	2.44	0.55	0.59	0.51	1.60	0.01
KC-163b	E2b	0.76	2.35	4.77	1.70	0.79	4.7	0.20	0.44	32.0	48.8	27.1	28.7	44.2	1.30	8.88	0.37	1.04	0.20	0.25	26.7	0.92	0.54	2.67	0.57	0.65	0.44	1.57	0.02
KC-63b	E3b	0.73	2.23	4.50	1.47	0.89	2.3	0.17	0.56	31.1	49.8	27.1	32.1	40.8	1.34	6.92	0.37	0.94	0.23	0.25	29.5	0.93	0.51	2.77	0.55	0.67	0.49	1.14	0.01

IV-b: Acid Data for PCA

			Normal and Isoprenoid Acids																										n-acid ratio	Hopanoic Acids (HA)					
		Variables->	n-C12	n-C13	n-C14	n-C15	n-C16	n-C17	n-C18	n-C19	n-C20	n-C21	n-C22	n-C23	n-C24	n-C25	n-C26	n-C27	n-C28	n-C29	n-C30	n-C31	n-C32	n-C33	n-C34	Pr-acid	Ph-acid	Tot.n-acids	nC28/nC18	C30 17α(H),	C31 17α(H),	C32 17α(H),	C33 17α(H),	Tot. HA
Sample ID	PC objects	Particle size	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20	A21	A22	A23	A24	A25	ATot	AP1	HA1	HA2	HA3	HA4	tHA
NS-oil	CO	n/a	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00	0	0	0	0	0
1-4a2	M1a	4mm-1mm	0	0	0	1099	3310	307	2869	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	301	660	2517	0.00	0	0	0	0	0
1-4b2	M1b	4mm-1mm	297	0	477	2199	8108	1103	5716	0	265	484	292	0	256	0	0	0	0	0	0	0	0	0	0	838	1041	13601	0.00	0	0	0	0	0
1-4c2	M1c	4mm-1mm	0	0	0	1328	599	384	4370	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	997	1723	0.00	0	0	0	0	0
1-4d2	M1d	4mm-1mm	0	0	568	2104	8873	1038	6729	434	416	0	0	0	0	0	0	0	0	0	0	0	0	0	0	644	904	12862	0.00	0	0	0	0	0
1-4e2	M1e	4mm-1mm	0	0	829	1408	697	507	3648	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	378	1000	0	0.00	0	0	0	0	0
1-4f2	M1f	4mm-1mm	0	0	748	1339	3969	799	3072	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	483	571	0	0.00	0	0	0	0	0
1-4g2ov	M1g	4mm-1mm	0	0	673	1335	4940	602	3389	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	393	830	0	0.00	0	0	0	0	0
63-1a2	M2a	1mm-63um	0	0	731	1454	4249	313	2971	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	319	464	82590	0.00	0	0	0	0	0
63-1b2	M2b	1mm-63um	295	0	754	1397	4894	0	2859	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	277	664	4680	0.00	0	0	0	0	0
63-1c2	M2c	1mm-63um	0	0	1305	1938	6832	753	4813	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	636	1057	5565	0.00	0	0	0	0	0
63-1d2	M2d	1mm-63um	314	0	875	1739	6173	518	3745	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	601	708	9452	0.00	0	0	0	0	0
63-1e2	M2e	1mm-63um	0	0	455	1275	2522	0	1014	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	511	0	5644	0.00	0	0	0	0	0
63-1f2	M2f	1mm-63um	218	285	1114	2030	4693	642	1437	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	707	746	0	0.00	0	0	0	0	0
63-1g2o	M2g	1mm-63um	340	268	1272	1831	7023	788	4469	0	301	0	0	0	0	0	0	0	0	0	0	0	0	0	0	760	1019	6154	0.00	0	0	0	0	0
63a2	M3a	<63um	0	0	783	1428	2687	0	1315	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1968	0.00	0	0	0	0	0
63b2	M3b	<63um	0	0	1126	1290	2074	550	1442	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1954	0.00	0	0	0	0	0
63c2	M3c	<63um	0	0	428	1234	2021	0	720	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	338	1375	0.00	0	0	0	0	0
63d2	M3d	<63um	0	0	477	2158	3931	0	1810	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	690	430	4973	0.00	0	0	0	0	0
63e2	M3e	<63um	0	0	603	1327	6741	0	1794	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	280	380	7866	0.00	0	0	0	0	0
63f2	M3f	<63um	343	497	1584	2799	8991	933	4755	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1012	1144	9095	0.00	0	0	0	0	0
63g2-ov	M3g	<63um	0	0	1014	2135	7149	615	3926	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	573	748	4145	0.00	0	0	0	0	0
1-4col2	C1	4mm-1mm	447	2423	5867	7445	15825	6870	11603	4090	3782	2648	4977	2862	8778	1521	3664	988	2671	1104	1991	901	1078	9792	1217	3099	3016	82590	0.23	256	360	1939	540	3095
63-1col2	C2	1mm-63um	3512	6541	12245	12948	27760	14700	22149	8618	8697	5437	11197	5252	19879	3044	9175	1833	5869	2038	4403	1051	2399	779	3257	8646	6191	189531	0.26	304	1122	7471	2386	11282
63col2	C3	<63um	2929	5611	8356	8014	17218	6743	10924	3737	3629	2295	4528	2261	7656	1257	4220	848	2215	907	1715	395	879	0	1729	3421	3208	92976	0.20	245	791	3832	1121	5989
KC-14	E1	4mm-1mm	146588	156471	182280	156296	269664	189255	211672	123410	122824	106418	150045	89405	178067	59037	58870	45530	59204	50838	53193	37819	37661	31345	51639	47897	59797	2646634	0.28	1728	31996	228135	64821	326680
KC-163	E2	1mm-63um	161370	147403	102302	99391	105820	140871	103597	70848	59504	86867	41950	21794	75099	67262	50588	31729	75386	68579	73816	13063	69026	19342	1157	154610	75913	1765661	0.73	0	11834	61459	13206	86498
KC-63	E3	<63um	319670	323274	244856	259147	555267	385971	327158	170787	338218	378018	188434	228855	304695	104423	125094	240040	237523	201110	274123	31224	235007	89137	100011	399642	186694	6157466	0.73	0	6542	47994	11653	66189

Appendix IV-b cont'd

List on CD ROM

All Biomarkers (Migration Study)I

All Biomarkers (Migration Study) II

All Biomarkers (Migration Study) III

Appendix IV-c: Rock Analysis and Characterisation

Rock Characterisation Analysis Data

Oil Show Analysis (Rock-Eval Pyrolysis)										
Sample ID	Wt (mg)	Tmax	True T-Peak	GAS (S0)	S1(OIL)	S2	HCGP	TPI	TOC %	HI, S2/TOC
Pyro Name						mg/g rock	S1+S2	S1/(S1+S2)		
STD	100.2	430	432.00	***	***	13.59		***	from TOC	
BLANK	***	***	***	***	***	***		***		
1-63umVICA	18.7	418	420.00	0.21	8.93	340.53	349.46	0.026	49.98	681.3325
1-63umVICB	18.5	421	423.00	0.10	7.56	318.91	326.47	0.023	50.08	636.8011
1mm-4mmVICA	18.4	419	421.00	0.05	9.51	333.15	342.66	0.028	51.87	642.2788
1mm-4mmVICB	18.6	421	423.00	0.05	8.27	326.45	334.72	0.025	52.62	620.3915
<63umVICA	17.6	419	421.00	0.00	7.38	288.18	295.56	0.025	44.3	650.5192
<63umVICB	19.1	417	419.00	0.00	8.32	283.35	291.67	0.029	44.85	631.7726

BET Analysis			
Sample Tube	Tube 1	Tube 2	Tube 3
Particle size	Coarse (4mm-1mr	Medium (1mm-	Fine (<63µm)
Wt. of raw sample + tube (g)	26.108	17.830	17.355
Wt. of tube + outgassed sample (g)	26.036	17.805	17.344
Wt. of sample tube assembly (g)	21.222	16.466	16.732
raw sample wt. (g)	4.886	1.364	0.623
Wt. of outgassed sample (g)	4.814	1.340	0.612
% impurities	1.480	1.803	1.701
Calc. BET (Specific surface) Area (m2/g)	4.467	4.400	9.625
total surface (BET) area	21.504	5.894	5.894

TOC	Extraction (EOM) Yield				
Sample	TOC (%)	Sample Wt	Wt of Extract	Extract Yield	CNE,mgExtr/gTOC
		g	g	mg/g	(%)
1 - 4 mm rep 1	51.87	40	1.2	30.00	57.84
1 - 4 mm rep 2	52.62	30	0.92	30.67	61.36
63µm - 1 mm rep 1	49.98	20	0.5	25.00	56.43
63µm - 1 mm rep 2	50.08	40	1.2	30.00	57.01
< 63µm rep 1	44.30	30	0.92	30.67	61.24
< 63µm rep 2	44.85	20	0.5	25.00	55.74

Appendix IV-c cont'd

List on CD ROM

Mercury Injection Porosimetry and Particle Density Measurements

Appendix IV-d: PCA (Multivariate Analysis) Data

List on CD ROM

Olefins & Biomarker Parameter Data Matrix for PCA

Acid Data Matrix for PCA

Olefins and Biomarker Parameter Normalised Data for PCA

Acid Normalised Data for PCA

IV-d: Olefins and Biomarker Parameter Resemblance Data for PCA

Euclidean Distance (Olefins + Biomarker Parameters)

Type	Crude oil		Migrated oils																										Column extract						Rock extract					
Variant	oil		4mm-1mm					1mm-63µm					<63µm					4mm-1mm					1mm-63µm		<63µm						4-1mm	1-63µm	<63µm	4-1mm	1-63µm	<63µm	4-1mm	1-63µm	<63µm	4-1mm	1-63µm	<63µm
Sample	O1	O2	M1a	M1b	M1c	M1d	M1e	M2a	M2b	M2c	M2d	M2e	M3a	M3b	M3c	M3d	M3e	M1f	M1g	M1h	M1i	M1j	M2f	M2g	M3f	M3g	M3h	M3i	M3j	C1a	C2a	C3a	C1b	C2b	C3b	E1a	E2a	E3a	E1b	E2b	E3b
O1																																									
O2	1.90																																								
M1a	4.68	4.30																																							
M1b	3.90	3.45	1.97																																						
M1c	4.90	4.46	2.18	1.62																																					
M1d	4.32	3.34	2.51	1.65	1.86																																				
M1e	5.45	4.62	3.73	3.24	2.93	2.63																																			
M2a	6.65	6.20	3.50	3.72	3.37	4.18	4.20																																		
M2b	4.72	3.99	3.92	3.06	2.95	2.70	1.99	4.39																																	
M2c	4.86	4.05	4.01	3.19	3.51	2.65	4.41	5.43	4.18																																
M2d	4.12	3.05	3.48	2.41	2.70	1.53	3.04	5.07	2.55	2.66																															
M2e	5.34	4.33	3.42	2.53	2.16	1.61	2.89	4.34	2.97	2.99	1.95																														
M3a	3.65	2.90	2.99	2.28	2.54	1.94	2.92	4.52	2.68	3.55	2.42	2.72																													
M3b	5.42	4.64	3.70	2.62	2.27	2.02	3.44	4.81	3.40	2.92	2.37	1.59	2.93																												
M3c	5.73	5.00	3.04	2.93	2.02	2.21	3.41	4.34	3.69	3.27	2.93	2.00	2.83	1.88																											
M3d	4.75	4.12	3.01	2.02	1.82	1.83	3.63	4.53	3.29	3.08	2.25	1.85	2.35	1.33	1.89																										
M3e	2.78	2.07	3.68	2.40	3.25	2.37	3.78	5.49	3.04	3.37	2.02	3.12	1.93	3.22	3.76	2.61																									
M1f	6.67	5.92	4.00	3.97	3.82	4.11	4.36	3.55	4.65	5.31	4.99	4.35	4.88	4.74	4.66	4.75	5.53																								
M1g	5.24	4.73	3.48	2.98	2.66	3.23	3.11	3.46	2.73	4.51	3.56	3.45	3.49	3.70	3.79	3.55	4.12	3.09																							
M1h	4.51	3.76	3.10	1.84	2.09	1.64	2.69	4.41	2.80	3.53	2.35	2.02	2.09	1.92	2.70	1.83	2.48	4.15	3.10																						
M1i	4.21	3.68	3.30	2.24	2.07	1.83	2.49	4.71	2.46	3.47	2.31	2.35	1.77	2.13	2.52	2.04	2.36	4.76	3.30	1.45																					
M1j	4.08	3.11	3.52	2.58	2.74	1.91	2.80	4.87	2.22	2.97	1.59	2.14	2.15	2.81	2.95	2.64	2.10	4.61	3.37	2.43	2.22																				
M2f	3.06	3.25	2.83	2.80	3.64	3.56	4.33	4.72	4.11	4.85	3.87	4.68	3.40	4.94	4.81	4.26	3.37	4.99	3.79	3.79	3.86	3.86																			
M2g	4.87	4.38	3.51	3.14	3.14	3.08	2.41	4.29	2.64	4.59	3.62	3.76	2.83	3.82	3.82	3.65	3.71	4.30	2.65	2.66	2.68	3.39	3.55																		
M3f	5.27	4.68	5.25	4.66	5.08	4.64	5.08	6.37	4.98	5.73	4.87	5.28	4.15	5.18	5.53	4.89	4.45	5.67	4.67	3.99	4.44	4.86	4.75	3.77																	
M3g	4.58	3.95	4.41	3.68	4.13	3.51	3.97	5.82	3.97	4.64	3.75	4.26	3.13	4.11	4.48	3.92	3.41	5.45	4.27	3.01	3.22	3.78	4.17	3.12	1.76																
M3h	4.76	4.32	4.49	4.03	4.21	3.86	4.22	5.99	4.15	4.79	4.21	4.58	3.29	4.35	4.41	4.12	3.81	5.43	4.25	3.40	3.32	3.92	4.35	3.05	2.22	1.50															
M3i	4.51	4.05	4.69	3.70	4.33	3.92	4.79	5.87	4.49	4.92	4.10	4.43	3.45	4.24	4.84	3.89	3.42	5.55	4.46	3.14	3.63	4.10	4.34	3.82	1.92	1.64	2.41														
M3j	4.64	4.04	4.01	3.28	3.43	3.27	3.03	4.96	2.87	5.45	3.52	3.67	2.92	3.84	4.28	3.49	3.35	4.91	3.25	2.50	2.78	3.61	3.82	2.71	4.08	3.55	3.92	3.75													
C1a	11.01	9.91	9.84	9.21	8.55	8.00	8.03	10.39	8.40	8.08	7.80	7.12	8.37	6.88	7.18	7.74	8.82	10.08	9.38	7.97	7.81	7.99	11.10	9.06	9.69	8.85	8.98	9.30	8.99												
C2a	11.14	10.10	10.21	9.49	8.80	8.35	8.33	10.65	8.54	8.63	8.09	7.36	8.59	7.12	7.52	7.93	8.97	10.29	9.51	8.18	8.02	8.23	11.34	9.30	9.95	9.20	9.30	9.51	8.97	2.16											
C3a	10.32	9.17	9.43	8.80	8.14	7.61	7.12	9.69	7.36	8.15	7.32	6.73	7.61	6.77	6.98	7.49	8.20	9.47	8.49	7.48	7.24	7.31	10.39	8.20	8.98	8.27	8.36	8.74	7.90	3.00	2.62										
C1b	5.43	4.17	4.74	4.08	4.25	3.17	4.16	6.01	3.86	3.75	2.80	3.39	3.64	3.56	3.88	3.77	3.74	5.37	4.51	3.68	3.83	2.97	5.12	4.58	5.07	4.29	4.60	4.76	4.61	7.25	7.80	6.81									
C2b	12.37	11.23	10.61	10.07	9.27	8.95	9.08	10.79	9.43	9.14	8.88	7.96	9.55	7.64	7.92	8.53	10.07	10.29	9.92	8.85	8.90	9.13	12.08	9.93	10.50	9.89	9.99	10.21	9.86	2.73	3.09	4.37	8.24								
C3b	8.75	7.84	7.20	6.61	5.88	5.69	5.90	7.76	6.15	6.22	5.77	4.92	5.82	4.41	4.63	5.10	6.53	7.39	6.63	5.29	5.27	5.78	8.48	6.31	6.86	6.23	6.21	6.52	6.43	3.79	4.08	4.05	5.36	4.35						
E1a	22.08	21.02	20.62	20.08	19.59	19.31	19.34	20.07	19.79	19.06	19.34	18.43	20.01	18.39	18.74	19.23	20.41	19.52	19.85	19.37	19.54	19.50	21.95	20.34	20.94	20.48	20.61	20.56	20.29	15.41	15.36	15.93	18.78	14.54	16.96					
E2a	21.93	21.01	20.44	19.90	19.54	19.33	19.50	19.95	19.81	19.10	19.36	18.59	20.05	18.51	18.87	19.23	20.36	19.52	19.73	19.42	19.62	19.56	21.66	20.33	20.55	20.09	20.25	20.10	20.31	16.45	16.50	16.94	18.97	15.69	17.50	8.13				
E3a	22.04	21.04	20.51	19.94	19.45	19.24	19.41	20.04	19.77	18.87	19.21	18.36	20.02	18.24	18.62	19.07	20.34	19.56	19.79	19.32	19.48	19.47	21.87	20.35	21.06	20.59	20.75	20.64	20.35	15.38	15.39	16.09	18.71	14.39	16.81	3.51	8.78			
E1b	18.83	18.25	17.67	17.20	17.18	17.16	17.29	16.74	17.43	17.16	17.36	16.86	17.66	16.77	17.20	17.31	18.09	16.45	16.78	17.21	17.47	17.55	18.23	17.68	18.55	18.29	18.45	18.16	17.69	17.73	17.80	17.44	16.75	17.30	17.31	14.90	14.28	14.77		
E2b	21.45	20.43	19.77	19.25	18.78	18.65	18.40	18.86	18.76	18.65	18.65	17.81	19.36	17.85	18.22	18.62	19.79	18.44	18.66	18.68	18.89	18.82	20.97	19.34	19.93	19.56	19.74	19.63	19.30	15.78	15.69	15.84	18.24	14.83	16.75	6.69	5.66	7.46	13.25	
E3b	21.18	20.25	19.61	19.09	18.78	18.60	18.81	19.17	19.13	18.39	18.67	17.99	19.32	17.84	18.24	18.56	19.69	18.61	18.88	18.71	18.91	18.93	20.84	19.60	20.12	19.71	19.87	19.71	19.62	16.31	16.43	16.73	18.23	15.54	17.07	8.56	6.34	8.13	11.84	6.89

IV-d: Acids Resemblance Data for PCA

Resemblance (Euclidean Distance) Data- Acids

Type	Crude oil	Migrated oils																				Column extract			Rock extract		
Variant	oil	4mm-1mm							1mm-63µm							<63µm							4-1mm	1-63µµm	<63µm	4-1mm	1-63µm	<63µm
Sample	O	M1a	M1b	M1c	M1d	M1e	M1f	M1g	M2a	M2b	M2c	M2d	M2e	M2f	M2g	M3a	M3b	M3c	M3d	M3e	M3f	M3g	Col1	Col2	Col3	Ext1	Ext2	Ext3
O																												
M1a	7.03																											
M1b	8.62	3.70																										
M1c	6.64	1.87	4.31																									
M1d	8.36	3.02	3.00	3.72																								
M1e	7.05	2.96	3.83	3.33	3.15																							
M1f	7.33	2.86	3.69	3.46	2.97	0.81																						
M1g	7.39	2.83	3.68	3.42	2.95	0.87	0.19																					
M2a	7.69	2.36	3.05	3.07	2.12	2.70	2.58	2.58																				
M2b	7.50	2.99	3.25	3.58	3.04	2.96	2.91	2.86	2.10																			
M2c	8.00	2.49	2.97	3.28	2.01	2.22	2.01	1.99	0.83	2.22																		
M2d	7.95	2.69	2.66	3.44	2.41	2.66	2.48	2.48	1.47	1.65	1.37																	
M2e	6.68	3.35	4.25	4.00	3.63	3.49	3.38	3.43	2.63	2.57	2.99	3.09																
M2f	7.59	3.49	3.70	4.06	3.50	2.04	1.84	1.85	3.16	2.88	2.71	2.48	3.83															
M2g	8.31	3.36	2.65	4.01	2.36	3.19	3.03	3.03	2.40	2.55	2.26	1.83	3.74	2.43														
M3a	6.51	3.83	4.69	3.63	4.09	3.78	3.71	3.73	3.17	3.04	3.52	3.61	1.88	4.18	4.20													
M3b	6.69	3.62	4.34	3.35	3.70	3.39	3.29	3.35	2.81	3.46	3.08	3.24	2.50	3.84	3.84	1.64												
M3c	6.46	3.12	4.20	2.76	3.56	3.05	3.10	3.05	2.56	2.29	2.84	3.02	2.67	3.59	3.66	1.93	2.54											
M3d	7.32	2.60	3.53	3.39	2.77	2.68	2.62	2.59	1.67	1.40	1.84	2.16	2.02	3.13	2.92	2.79	3.26	2.04										
M3e	7.31	2.66	3.54	3.36	2.77	2.82	2.70	2.65	1.61	1.37	1.85	2.16	2.01	3.22	2.92	2.61	3.10	1.85	0.44									
M3f	8.46	3.27	3.01	3.98	2.80	3.10	2.91	2.91	2.15	2.36	1.97	1.46	3.65	2.18	1.34	4.16	3.77	3.60	2.75	2.76								
M3g	7.90	2.39	2.98	3.20	2.02	2.16	1.93	1.91	0.81	2.16	0.20	1.36	2.85	2.64	2.27	3.38	2.96	2.74	1.75	1.76	1.98							
Col1	13.08	9.84	8.44	10.16	8.93	9.77	9.69	9.69	9.37	9.53	9.31	9.22	10.03	9.43	8.86	10.28	10.05	10.04	9.64	9.65	9.00	9.33						
Col2	14.16	10.83	9.30	11.17	9.86	10.74	10.66	10.66	10.34	10.45	10.25	10.12	11.03	10.34	9.73	11.31	11.07	11.07	10.62	10.63	9.86	10.28	1.49					
Col3	13.01	9.71	8.20	10.04	8.76	9.61	9.53	9.53	9.20	9.30	9.13	8.98	9.88	9.18	8.59	10.13	9.90	9.89	9.48	9.49	8.72	9.15	2.54	2.10				
Ext1	18.36	14.92	13.26	15.25	13.84	14.80	14.70	14.69	14.38	14.47	14.26	14.11	15.13	14.32	13.68	15.38	15.13	15.16	14.68	14.70	13.78	14.29	5.48	4.33	5.94			
Ext2	17.49	14.04	12.39	14.42	12.98	13.92	13.83	13.83	13.51	13.59	13.39	13.23	14.28	13.42	12.78	14.59	14.34	14.34	13.81	13.84	12.88	13.42	5.75	4.87	6.22	4.23		
Ext3	19.18	15.59	13.87	15.99	14.48	15.50	15.39	15.37	15.05	15.15	14.91	14.77	15.85	14.99	14.31	16.16	15.91	15.91	15.36	15.38	14.41	14.96	7.10	6.16	7.61	4.26	2.16	

Appendix IV-d cont'd

List on CD ROM

Olefins and Biomarker Parameter Transformed Data for PCA

Acids Transformed Data for PCA

IV-d: PCA Scores for Olefins and Biomarker Parameters

PCA Scores (Olefins and Biomarker Parameters					
Mig. Samples	**SCORE1**	**SCORE2**	**SCORE3**	**SCORE4**	**SCORE5**
O1	5.3740	1.5725	0.4967	0.2964	-2.6459
O2	4.4136	1.0061	0.4090	0.1912	-2.3364
M1a	3.8571	1.5022	0.1438	1.3933	0.6318
M1b	3.4006	1.3056	0.1540	0.9182	-0.0984
M1c	2.9295	0.6417	-0.1321	1.0929	0.7971
M1d	2.7850	0.2965	0.0022	0.7838	-0.2318
M1e	2.7190	0.0662	-0.1837	0.1907	1.2569
M2a	2.9449	2.2901	-0.4126	1.4626	2.7989
M2b	3.1121	0.2360	-0.2073	0.0498	0.6662
M2c	2.3653	0.2059	0.0475	1.4125	-1.4459
M2d	2.7668	-0.0730	0.0144	0.6070	-0.8951
M2e	1.9217	-0.3425	-0.2188	0.9388	0.1747
M3a	3.5055	0.1756	-0.0301	0.0237	-0.4832
M3b	1.8197	-0.5004	-0.3154	0.5866	-0.1144
M3c	2.1524	-0.5838	-0.3326	1.0320	0.4970
M3d	2.6402	-0.1847	-0.0471	0.7537	-0.2130
M3e	3.8684	0.2086	0.3277	0.2840	-1.5659
M1f	2.4707	2.1325	-0.1183	0.9261	2.3863
M1g	2.9779	1.4845	-0.1311	0.1434	1.5971
M1h	2.8511	0.1338	0.0619	0.1077	0.0986
M1i	3.0280	-0.1732	-0.0884	0.1307	-0.1556
M1j	2.9853	-0.0808	0.0643	0.5846	-0.5413
M2f	5.1806	2.3237	0.3080	0.5067	-0.3419
M2g	3.6731	0.6390	0.1360	-0.4712	1.1879
M3f	4.0599	0.3275	1.8563	-2.1599	0.0452
M3g	3.7691	0.0288	1.5967	-1.5799	-0.2696
M3h	3.8951	-0.0488	1.5510	-1.6027	-0.0594
M3i	3.7616	0.4210	1.6894	-1.5766	-0.5302
M3j	3.6091	0.4207	-0.0104	-0.7647	0.7113
C1a	-1.9807	-5.6044	-1.3613	-1.0240	-0.4204
C2a	-2.0916	-5.7912	-1.4914	-1.1984	-0.2623
C3a	-1.3612	-4.8259	-1.4704	-1.7881	0.2585
C1b	2.0558	-0.3344	-0.6944	-0.4207	-1.0892
C2b	-3.1595	-5.6139	-1.5943	-0.8808	1.0146
C3b	-0.0056	-3.5552	-0.8659	-1.1208	0.5884
E1a	-16.0102	-1.9009	-0.2818	2.1724	-0.5662
E2a	-15.7679	0.9273	4.2536	-1.2471	-0.2225
E3a	-15.9244	-1.8339	-1.1104	3.0259	-1.0735
E1b	-10.1810	9.4133	-5.3468	-2.7965	-0.5971
E2b	-15.2725	0.8936	2.0024	-0.5100	2.4031
E3b	-15.1385	2.7947	1.3296	-0.4732	-0.9543

IV-d: PCA Scores for Acid Variables

PCA Scores (Olefins and Biomarker Parameters					
	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
O	5.3523	5.8995	1.3894	-0.5938	0.0516
M1a	2.7852	-0.0738	0.4133	0.1589	1.6799
M1b	0.9555	-1.0189	0.1292	0.1593	0.7724
M1c	3.0865	0.5949	0.2477	0.1341	2.0520
M1d	1.6469	-1.1448	-0.1297	0.1931	0.7183
M1e	2.7063	-0.2284	1.3263	0.5574	-0.6016
M1f	2.6137	-0.5017	1.1711	0.5692	-0.6933
M1g	2.6016	-0.5602	1.1518	0.5751	-0.6386
M2a	2.3256	-0.8049	-0.5083	-0.1190	0.4498
M2b	2.3937	-0.5582	-0.5211	-0.3984	-0.3191
M2c	2.1942	-1.1775	-0.0302	0.1579	0.1383
M2d	2.0371	-1.1006	0.0412	0.0277	0.0603
M2e	3.0241	0.5085	-1.3180	-0.7774	-0.7643
M2f	2.1429	-0.6056	1.5200	0.5286	-1.2142
M2g	1.4997	-1.2237	0.3617	0.1640	-0.0538
M3a	3.2734	0.9538	-1.6960	-0.8112	-0.6946
M3b	3.0314	0.6727	-1.0287	-0.3680	-0.3926
M3c	3.1195	0.6211	-0.8431	-0.4606	-0.0094
M3d	2.6317	-0.4163	-0.6615	-0.3849	-0.1643
M3e	2.6532	-0.3809	-0.8300	-0.4244	-0.1525
M3f	1.6130	-1.4500	0.2845	0.1416	-0.2729
M3g	2.2474	-1.0800	-0.0503	0.1322	0.1081
Col1	-6.6308	1.4150	-0.4147	0.8691	0.0987
Col2	-7.7171	1.1143	-0.4226	1.0491	0.0179
Col3	-6.3423	1.1942	-0.5185	1.3770	-0.0985
Ext1	-11.8361	0.3860	-0.8212	1.5280	-0.1860
Ext2	-10.9097	-0.2292	0.9685	-1.9804	0.0177
Ext3	-12.4987	-0.8053	0.7894	-2.0044	0.0909

IV-d: Principal Component Data (Olefins and Biomarker Parameters)

Principal Components (olefins +parameters)					
PCs	1	2	3	4	5
Eigenvalues	42	6.62	1.91	1.46	1.29
%Variation	73.7	11.6	3.3	2.6	2.3
Cum.%Variation	73.7	85.3	88.6	91.2	93.4
Eigenvectors (Coefficients in the linear combinations of variables making up PC's)					
Variable	PC1	PC2	PC3	PC4	PC5
P1	0.14	-0.134	0.004	-0.021	0.082
P2	-0.146	0.112	0.026	0.007	-0.045
P3	-0.147	0.11	0.028	0.004	-0.052
P4	0.148	-0.075	0.04	0.003	0.037
P5	0.009	0.027	-0.606	0.344	-0.103
P6	0.147	-0.103	-0.01	-0.039	0.07
P7	0.144	-0.058	0.064	-0.061	-0.042
P8	0.14	-0.08	0.035	-0.093	-0.123
P9	0.086	-0.154	0.021	-0.287	-0.415
P10	-0.138	0.086	-0.079	0.15	0.207
P11	0.142	-0.105	0.02	-0.047	0.048
P12	0.003	-0.096	0.102	0.191	-0.654
P13	-0.135	0.114	-0.045	0.019	0.116
P14	-0.118	0.117	-0.07	0.246	0.305
P15	0.091	-0.051	0.163	-0.317	0.203
P16	0.134	-0.115	-0.046	-0.065	0.087
P17	0.148	-0.088	-0.04	-0.013	0.044
P18	0.148	-0.078	-0.003	0.012	0.011
P19	0.142	-0.119	-0.034	0.025	0.121
P20	0.148	-0.101	-0.024	-0.003	0.039
P21	-0.146	0.113	0.041	0.014	-0.051
P22	0.146	-0.104	-0.028	0.015	0.072
P23	-0.144	0.112	0.014	-0.048	-0.014
P24	0.136	-0.061	0.039	-0.02	-0.01
P25	0.135	-0.103	0.038	-0.013	0.018
P26	-0.146	0.084	-0.056	-0.06	-0.065
P27	-0.144	0.111	0.017	-0.029	-0.05
P28	0.109	0.059	0.037	0.248	-0.27
H1	-0.133	-0.173	0.126	0.056	0.022
H2	0.003	-0.299	-0.257	0.254	-0.076
H3	-0.132	-0.168	0.172	0.092	0.029
H4	-0.012	-0.304	-0.175	0.245	0.094
H5	-0.127	-0.169	0.213	0.141	0.053
H6	0.103	-0.246	-0.179	-0.138	0.073
H7	-0.129	-0.164	0.199	0.131	0.043
H8	-0.077	-0.267	0.092	0.136	0.085
H9	-0.131	-0.165	0.174	0.12	0.031
H10	0.092	-0.263	-0.199	-0.165	0.07
H11	-0.132	-0.164	0.165	0.103	0.021
HT	-0.118	-0.197	0.238	0.143	0.033
D1	-0.143	-0.141	0.031	-0.012	-0.02
D2	-0.146	-0.12	0.039	-0.012	-0.015
D3	-0.149	-0.05	-0.105	-0.117	-0.017
D4	-0.15	-0.038	-0.101	-0.106	-0.014
D5	-0.143	-0.138	0.065	0.01	-0.012
D6	-0.148	-0.079	-0.097	-0.096	-0.038
D7	-0.149	-0.062	-0.096	-0.097	-0.028
D8	-0.148	-0.056	-0.09	-0.146	-0.035
D9	-0.149	-0.049	-0.112	-0.122	-0.022
D10	-0.145	-0.112	-0.045	-0.104	-0.013
D11	-0.147	-0.063	-0.122	-0.154	-0.013
D12	-0.145	-0.126	0.001	-0.057	-0.012
D13	-0.146	-0.076	-0.118	-0.14	-0.012
D14	-0.146	-0.094	-0.09	-0.112	-0.013
D15	-0.145	-0.087	-0.082	-0.147	-0.017
D16	-0.147	-0.061	-0.119	-0.141	-0.017
DT	-0.149	-0.062	-0.098	-0.116	-0.025

IV-d: Principal Component Data (Acids)

PCA- Principal Component Analysis (Acids only)					
PC	1	2	3	4	5
Eigenvalues	26.6	2.02	0.744	0.664	0.467
%Variation	83	6.3	2.3	2.1	1.5
Cum.%Variation	83	89.3	91.6	93.7	95.2
Eigenvectors (Coefficients in the linear combinations of variables making up PC's)					
Variable	PC1	PC2	PC3	PC4	PC5
A1	-0.17	-0.065	0.135	-0.035	-0.118
A2	-0.18	0.014	0.142	0.024	-0.172
A3	-0.148	-0.243	-0.167	-0.033	-0.7
A4	-0.157	-0.368	-0.176	-0.018	-0.037
A5	-0.143	-0.438	-0.222	0.018	-0.082
A6	-0.148	-0.185	0.402	0.272	0.227
A7	-0.148	-0.417	-0.099	0.079	0.131
A8	-0.187	0.072	-0.019	0.011	0.067
A9	-0.182	0.016	0.018	0.02	0.139
A10	-0.188	0.064	0.018	-0.039	0.076
A11	-0.188	0.081	-0.011	0.032	0.067
A12	-0.192	0.099	-0.011	-0.008	-0.012
A13	-0.189	0.084	-0.011	0.03	0.063
A14	-0.192	0.092	0.009	-0.053	-0.013
A15	-0.191	0.105	-0.01	0	-0.012
A16	-0.192	0.083	0.019	-0.082	-0.011
A17	-0.192	0.095	0.008	-0.049	-0.01
A18	-0.192	0.084	0.023	-0.091	-0.011
A19	-0.192	0.091	0.015	-0.067	-0.01
A20	-0.192	0.092	-0.002	-0.03	-0.014
A21	-0.192	0.083	0.027	-0.1	-0.009
A22	-0.18	0.063	0.045	-0.172	0.007
A23	-0.19	0.104	-0.043	0.067	-0.016
A24	-0.148	-0.289	0.25	0.05	-0.161
A25	-0.139	-0.311	0.371	0.183	0.319
ATot	-0.134	-0.15	-0.592	-0.235	0.468
HA1	-0.131	0.199	-0.313	0.762	-0.046
HA2	-0.191	0.101	-0.02	0.022	-0.021
HA3	-0.191	0.105	-0.025	0.036	-0.019
HA4	-0.191	0.103	-0.028	0.041	-0.021
tHA	-0.191	0.108	-0.028	0.044	-0.019
AP1	-0.18	0.035	0.155	-0.406	0.01

IV-d: Principal Component Data (Acids)

Eigenanalysis of the Correlation Matrix for selected Sat HCs observations					
Eigenvalue	44.322	9.654	2.291	1.070	0.773
Proportion	0.715	0.156	0.037	0.017	0.012
Cumulative	0.715	0.871	0.908	0.925	0.937
Variable	PC1	PC2	PC3	PC4	PC5
n-C12	0.125	-0.071	0.010	0.082	-0.065
n-C13	0.144	-0.060	0.034	0.068	-0.006
n-C14	0.146	-0.057	0.038	0.055	0.007
n-C15	0.146	-0.058	0.034	0.049	0.005
n-C16	0.147	-0.059	0.039	0.046	0.007
n-C17	0.147	-0.057	0.039	0.048	0.001
Pristane	0.146	-0.058	0.037	0.057	0.016
n-C18	0.147	-0.056	0.040	0.038	-0.003
Phytane	0.144	-0.054	0.032	0.037	-0.014
n-C19	0.147	-0.056	0.042	0.043	-0.002
n-C20	0.147	-0.057	0.040	0.047	-0.010
n-C21	0.147	-0.057	0.045	0.059	-0.008
n-C22	0.147	-0.058	0.043	0.053	-0.002
n-C23	0.147	-0.056	0.029	0.063	-0.014
n-C24	0.147	-0.059	0.023	0.063	-0.007
n-C25	0.147	-0.057	-0.004	0.074	-0.006
n-C26	0.146	-0.061	-0.043	0.069	0.018
n-C27	0.145	-0.049	-0.123	0.064	0.014
n-C28	0.142	-0.043	-0.181	0.048	0.034
n-C29	0.133	-0.031	-0.286	0.037	0.046
n-C30	0.129	-0.024	-0.326	0.002	0.042
n-C31	0.115	-0.010	-0.399	-0.011	0.051
n-C32	0.104	-0.005	-0.456	0.002	0.069
n-C33	0.076	-0.011	-0.455	-0.201	0.158
n-C34	0.120	-0.062	-0.148	-0.019	-0.021
n-C35	0.114	0.003	0.019	0.064	-0.555
nC36	0.090	0.061	-0.162	0.252	-0.676
C27Ts	0.135	0.122	0.028	0.060	0.060
C27Tm	-0.127	0.118	-0.086	0.040	-0.039
28,30-BNH	0.090	0.207	0.069	-0.137	-0.025
C29, 25nor17a-	0.135	0.061	0.098	-0.032	-0.000
C29,ab30nor	-0.134	0.135	-0.072	0.003	-0.049
C29Ts	0.078	0.262	0.012	0.003	0.030
C30*17a-diahop	0.143	0.082	0.063	-0.064	0.015
C29ba-norhop	-0.133	0.124	-0.081	-0.043	-0.092
C30ab hop	0.120	0.185	0.017	0.002	0.047
C30ba-hop	-0.131	0.124	-0.085	-0.059	-0.084
C31-22SHop	0.138	0.120	0.040	-0.078	0.009
C31-22RHop	-0.005	0.312	-0.060	-0.094	-0.098
Gamm	-0.138	0.116	-0.063	-0.060	-0.075
C31ba22S+R	-0.134	0.127	-0.080	-0.063	-0.088
C32 22S	0.143	0.085	0.035	-0.096	0.003
C32 22R	0.133	0.130	0.028	-0.187	-0.021
C32ba22S+R	0.107	0.138	0.007	-0.425	-0.128
C33 22S	0.145	0.064	0.036	-0.111	-0.037
C33 22R	0.129	0.120	0.022	-0.263	-0.077
C34 22S	0.142	0.081	0.053	-0.139	-0.009
C34 22R	0.132	0.120	0.044	-0.191	-0.067
C35 22S	0.131	0.137	0.031	-0.098	-0.043
C35 22R	0.134	0.125	0.053	-0.041	-0.010
C27aaa20S	-0.047	0.283	-0.005	0.170	0.054
C27abb20R	0.141	0.075	0.075	0.077	0.081
C27abb20S	0.135	0.070	-0.008	0.148	0.079
C27aaa20R	-0.135	0.124	-0.089	0.064	-0.021
C28aaa20S	0.100	0.200	0.045	0.080	0.006
C28abb20R	0.085	0.227	0.010	0.258	0.173
C28abb20S	-0.021	0.307	-0.040	0.174	0.062
C28aaa20R	-0.126	0.163	-0.083	0.044	0.026
C29aaa20S	0.078	0.177	0.042	-0.049	0.207
C29abb20R	0.009	0.232	-0.004	0.477	0.072
C29abb20S	0.117	0.155	0.097	0.005	0.102
C29aaa20R	-0.140	0.094	-0.102	0.040	-0.044

Appendix IV-e

Brief Explanation of the Principal Component Analysis (PCA) Method

First formulated in statistics by Pearson (1901), principal component analysis (PCA) forms the basis of multivariate analysis (Wold et al., 1987). Its rediscovery, utility in many more diverse disciplines, and subsequent development over several decades by numerous scholars (e.g. Davis and Sampson, 2002, Malinowski, 1991) have paved ways for development design production of various application packages used for the implementation of this multivariate statistical technique, and the continuous improvements on led to breakthrough. In terms of application, its goal is to reduce the dimension of large amounts of data having interrelated variables while retaining most of the variation present in all of the original variables (Wold et al., 1987, Farrimond et al., 1994). PCA provides an approximation of a data matrix; extracts important information from transformed data, represented as a set of new orthogonal variables called principal components (Clarke, 1993, Wold et al., 1987). This uncorrelated set of new variables is ordered so as that the first few retain most of the variation present in the initial set of variables.

Data set

The input data set consisted of a data matrix or table, X, having N-rows (objects) and K-columns (variables). The 'objects' are the oil and rock extracts samples while the variables include biomarker compounds and parameters, olefinic and acidic markers, all measured on different scales, for each 'object', from measured peak areas in corresponding mass chromatograms. Replicate data were not obtained for all the acids due to the laborious nature of their analysis. Hence the acid data from the migration study were analysed separately as they do not share the same number of objects (samples) with olefins and the rest of the compounds. The selected biomarker parameters data were presented together with those of the olefins. Five 'migrated' oil samples from the duplicate 1mm-63μm particle size subset were omitted due to poor peak resolution and difficulties in peak integration for most of the entire variables. In all, 58 variables (29 biomarker parameters and 29 olefinic compounds) for 41 objects (including the initial North Sea oil, rock extracts and replicate 'migrated' oil aliquots), and 32 other variables (acidic compounds) for 28 samples (crude oil, rock extracts and 'migrated' oil aliquots). Consequently, the samples variables are split into few subsets for ease of analysis and data interpretation from the plots.

Descriptive statistical report for the migration (olefins and biomarker parameters) Dataset

Variable	Total Count	Mean	SE Mean	StDev	Minimum	Median	Maximum	Range	Skewness
H1	41	5708	2386	15275	0	14	54264	54264	2.47
H2	41	167.4	76.4	488.9	0.0	27.5	2616.7	2616.7	4.24
H3	41	1371	564	3612	0	18	12553	12553	2.49
H4	41	57.1	16.7	106.7	0.0	20.4	577.7	577.7	3.63
H5	41	433	170	1091	0	24	3890	3890	2.53
H6	41	27.85	6.25	40.03	0.00	16.35	171.52	171.52	2.73
H7	41	349	139	888	0	17	3241	3241	2.52
H8	41	66.4	21.7	139.0	0.0	13.3	555.6	555.6	2.87
H9	41	233.5	92.1	589.6	0.0	9.9	2111.1	2111.1	2.53
H10	41	20.64	5.25	33.63	0.00	11.26	139.97	139.97	2.82
H11	41	253	103	662	0	9	2638	2638	2.71
HT	41	8688	3528	22588	0	188	81372	81372	2.51
D1	41	5340	2281	14604	65	177	57235	57170	3.09
D2	41	22488	9092	58215	278	822	214624	214346	2.76
D3	41	8209	2959	18949	23	138	59314	59291	2.11
D4	41	37369	13450	86125	173	808	254545	254372	2.08
D5	41	17894	7220	46230	257	788	188349	188092	2.84
D6	41	12535	4911	31444	85	311	138088	138003	2.91
D7	41	59090	22273	142614	404	1573	557532	557128	2.60
D8	41	18619	6973	44650	36	136	153425	153388	2.26
D9	41	53617	19270	123389	237	837	386969	386732	2.10
D10	41	40131	16389	104941	49	176	394131	394082	2.63
D11	41	61407	22516	144175	30	165	451020	450989	2.09
D12	41	14073	5639	36105	58	189	134572	134514	2.58
D13	41	35617	13114	83971	55	278	298905	298851	2.36
D14	41	6993	2829	18115	16	84	78627	78611	2.95
D15	41	58327	22834	146211	50	194	498821	498770	2.42
D16	41	21354	7851	50271	21	95	167469	167449	2.15
DT	41	760319	288779	1849089	1854	6842	6528886	6527033	2.34
P1	41	1.1746	0.0284	0.1821	0.7292	1.2380	1.3441	0.6150	-1.90
P2	41	0.8019	0.0991	0.6343	0.5296	0.5432	2.3750	1.8454	2.08
P3	41	1.112	0.238	1.523	0.467	0.493	4.920	4.453	2.08
P4	41	3.505	0.133	0.852	1.455	3.836	4.228	2.774	-1.78
P5	41	0.88244	0.00723	0.04629	0.71795	0.88325	1.00000	0.28205	-0.74
P6	41	47.48	2.93	18.77	1.89	54.35	60.62	58.73	-2.03
P7	41	1.0117	0.0616	0.3944	0.1626	1.1321	1.5526	1.3899	-1.16
P8	41	1.2937	0.0599	0.3839	0.4030	1.4086	1.7167	1.3137	-1.38
P9	41	36.349	0.481	3.078	30.772	36.483	43.059	12.287	0.13
P10	41	33.39	1.11	7.11	25.09	31.27	49.82	24.73	1.44
P11	41	36.685	0.655	4.196	26.557	38.201	42.442	15.885	-1.63
P12	41	31.209	0.155	0.994	28.691	31.393	33.397	4.706	-0.63
P13	41	32.106	0.675	4.321	28.078	30.284	44.178	16.100	1.66
P14	41	0.9104	0.0313	0.2007	0.6738	0.8392	1.3379	0.6641	0.95
P15	41	26.90	4.91	31.45	4.46	15.18	184.57	180.11	3.55
P16	41	2.163	0.143	0.913	0.347	2.118	3.574	3.228	-0.76
P17	41	4.404	0.238	1.524	0.655	4.851	6.094	5.439	-1.78
P18	41	4.433	0.304	1.944	0.201	4.988	7.239	7.038	-1.32
P19	41	0.7340	0.0336	0.2150	0.1885	0.8114	0.9615	0.7729	-1.98
P20	41	51.86	1.53	9.79	26.74	55.81	56.52	29.78	-2.08
P21	41	0.2599	0.0451	0.2886	0.1119	0.1489	0.9777	0.8659	2.07
P22	41	1.8767	0.0889	0.5692	0.5123	2.0990	2.3416	1.8293	-1.91
P23	41	1.2455	0.0769	0.4923	0.9505	1.0405	2.7717	1.8212	2.22
P24	41	0.62536	0.00551	0.03531	0.50269	0.63468	0.66413	0.16144	-1.80
P25	41	0.9186	0.0205	0.1313	0.5878	0.9307	1.0795	0.4917	-1.30
P26	41	0.1581	0.0200	0.1279	0.0808	0.1021	0.5072	0.4264	2.03
P27	41	0.3032	0.0741	0.4745	0.0306	0.1219	1.7303	1.6997	2.18
P28	41	1.888	0.283	1.815	0.005	1.223	7.486	7.482	1.37

Olefin distributions are not normal, with highly skewed (positively) data; many of the biomarker parameters are normally distributed with some symmetric data (see close mean/median values; Minitab16)

Descriptive statistical report for the migration (acids) Dataset

Variable	Total Count	Mean	SE Mean	StDev	Minimum	Median	Maximum	Range	Skewness
A1	28	22726	13377	70783	0	0	319670	319670	3.43
A2	28	22956	13415	70983	0	0	323274	323274	3.47
A3	28	20419	11046	58450	0	806	244856	244856	3.18
A4	28	20646	10904	57696	0	1785	259147	259147	3.40
A5	28	39001	21565	114111	0	5556	555267	555267	4.01
A6	28	26938	15628	82694	0	608	385971	385971	3.64
A7	28	26927	13767	72846	0	3696	327158	327158	3.46
A8	28	13640	7656	40512	0	0	170787	170787	3.20
A9	28	19201	12745	67439	0	0	338218	338218	4.35
A10	28	20792	14072	74462	0	0	378018	378018	4.47
A11	28	14337	8467	44803	0	0	188434	188434	3.43
A12	28	12515	8645	45744	0	0	228855	228855	4.39
A13	28	21230	12499	66136	0	0	304695	304695	3.66
A14	28	8448	4732	25040	0	0	104423	104423	3.06
A15	28	8986	5082	26893	0	0	125094	125094	3.58
A16	28	11463	8685	45957	0	0	240040	240040	4.91
A17	28	13674	8940	47304	0	0	237523	237523	4.33
A18	28	11592	7627	40358	0	0	201110	201110	4.26
A19	28	14616	10123	53564	0	0	274123	274123	4.59
A20	28	3016	1753	9276	0	0	37819	37819	3.25
A21	28	12359	8694	46004	0	0	235007	235007	4.58
A22	28	5371	3371	17837	0	0	89137	89137	4.25
A23	28	5679	3948	20890	0	0	100011	100011	4.08
A24	28	22383	15083	79811	0	587	399642	399642	4.38
A25	28	12447	7267	38454	0	789	186694	186694	3.94
ATot	28	396822	240388	1272013	0	5605	6157466	6157466	3.95
HA1	28	90.5	62.7	331.9	0.0	0.0	1727.6	1727.6	4.79
HA2	28	1880	1212	6411	0	0	31996	31996	4.28
HA3	28	12530	8436	44640	0	0	228135	228135	4.55
HA4	28	3347	2359	12480	0	0	64821	64821	4.78
tHA	28	17848	12053	63781	0	0	326680	326680	4.58
AP1	28	0.0868	0.0379	0.2007	0.0000	0.0000	0.7277	0.7277	2.60

The acid dataset is not normally distributed; entire data is positively skewed data (PRIMER6).

The whole data set table, shown in AppendixIV-A and B, was analysed in subsets using the PCA multivariate analysis tool in Minitab and Primer6 statistical analysis package. Based on rather different starting point (the original data matrix) and assumptions about the definition of (dis)similarity of two samples, the principal component technique was used to understand the covariance structure in the original variables and form smaller number of uncorrelated variables (PCs) using this structure. The analysis culminates to a 2-3D ordination plot which approximates the continuum of relationships between samples.

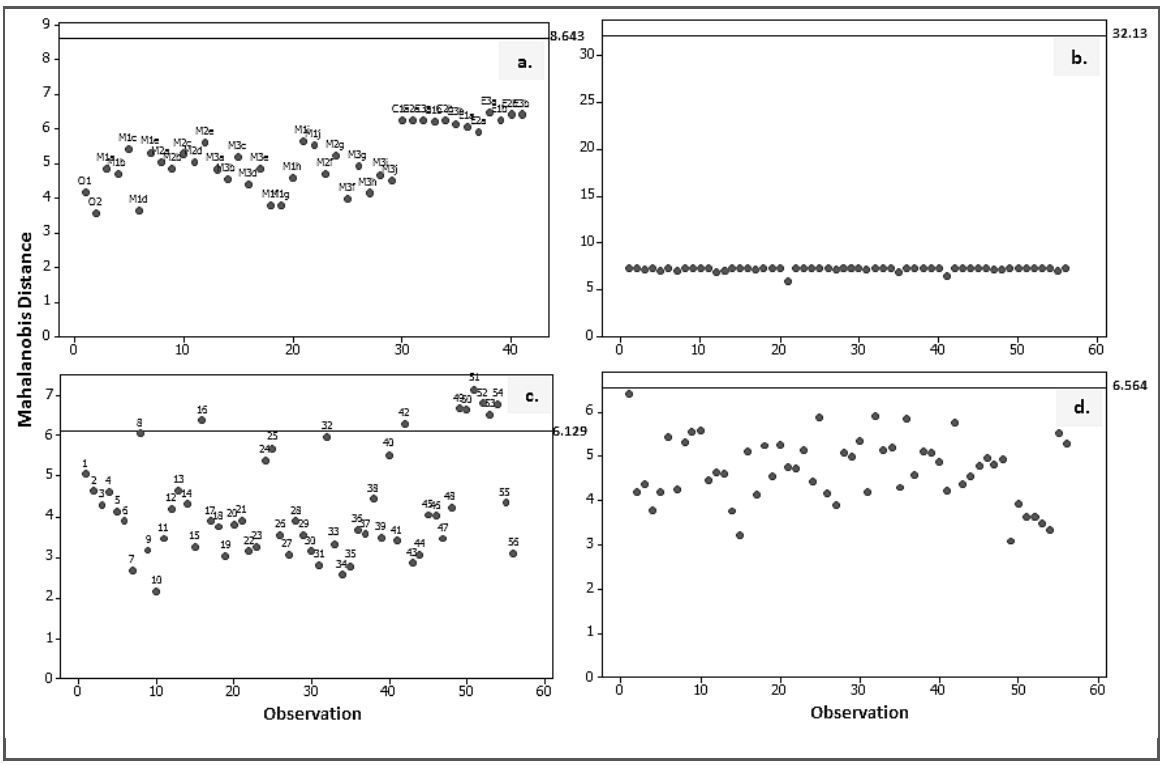
Resulting PC models from both applications were very similar as data transformation and/or standardization methods in both applications were comparable. The results presented in this session are from either software. In both cases data pre-treatment was performed as required for the transformation and scaling of the data matrix on which a polished PC model depends (Farrimond et al., 1994, Wold et al., 1987). Plots of a selection of variables against each other as scatter plots were first performed as a diagnostic screen prior to data normalisation using

the Draftsman plot (Clarke and Gorley, 2006), which calculates Pearson correlation coefficients between all pairs of variables. This check was necessary for meaningful PCA plots where correlations are an indication of highly correlated (say >0.95) variable pairs.

Data Pre-treatment

Being mainly chromatographic, and comprising of compounds and ratios which are measured on large scale differences, the data were first transformed using the logarithmic factor (Log [X+1]) in order to down-weight high abundance species as well as symmetrically distribute the data matrix. The transformed data were then normalised (subtract mean and divide by standard deviation) in order to auto-scale and centre them (Wold et al., 1987). Transformed data also allow for derivation of meaningful distances between samples, useful for determining similarities (Clarke and Gorley, 2006).

Being a list square method, models from PCA are greatly influenced by outliers. These were checked and eliminated prior to development of the final model. The Mahalanobis distance plot for each data point was used to identify outliers in multivariate space; a point beyond the indicated reference line represents an unusual observation. Following the observation in the present representative output plots, it is concluded that no outliers, except in the TAS and MAS variables, were observed as could be observed in the plots below.



Example Mahalanobis distance plots shown for a) olefins; b) Aromatic hydrocarbons; c) Aromatic steroid HCs; and d) n-alkanes variable subsets in the present data. They are powerful method for detecting outliers; any point above the Y-axis reference line, as shown above, is an outlier (Minitab16).

Due to the large amount of data available from the migration experiments, the task of representation of numerous variables in any model, and the limitation of lack of strong variability between the original oil and its 'migrated' portions, a multivariate statistical PCA method is employed here to reveal occurring variability and interpret this seemingly complex data. Output data from PCA of entire data matrix or its subsets are presented as points on fewer plots or graphs which display the pattern of similarity of the observations and of the variables (Clarke and Gorley, 2006). Inferences and important information are thereby drawn from these plots, and discussed in later sections. Relevant generated data tables, plots, graphs and diagrams are presented in the Appendix IV. Where references are made to these plots or diagrams in the text and are not represented within related sessions of this chapter, references to them contained in designated appendix and are indicated.

Analyses

The pre-treated data worksheet was then used to create lower triangular resemblance matrix in the resemblance analysis. Resemblances between observations (samples) are calculated by default in the PRIMER6 (P6) application regardless of data (column-row) orientation. Based on the type of data (chromatographic), the Euclidean distance measure was used. The P6 package computes the Euclidean distance d(i, j) between any objects 'i' and 'j' where measurements are taken on an interval scale (Clarke, 1993). The resemblance worksheets derived from the analyses of the transformed sample worksheets for acids, and olefins – selected biomarker parameters are represented in the triangular matrices represented in Apendix IV-d. The resemblance matrix is required as input data by other analyses such as the hierarchical clustering technique (Clarke and Gorley, 2006)

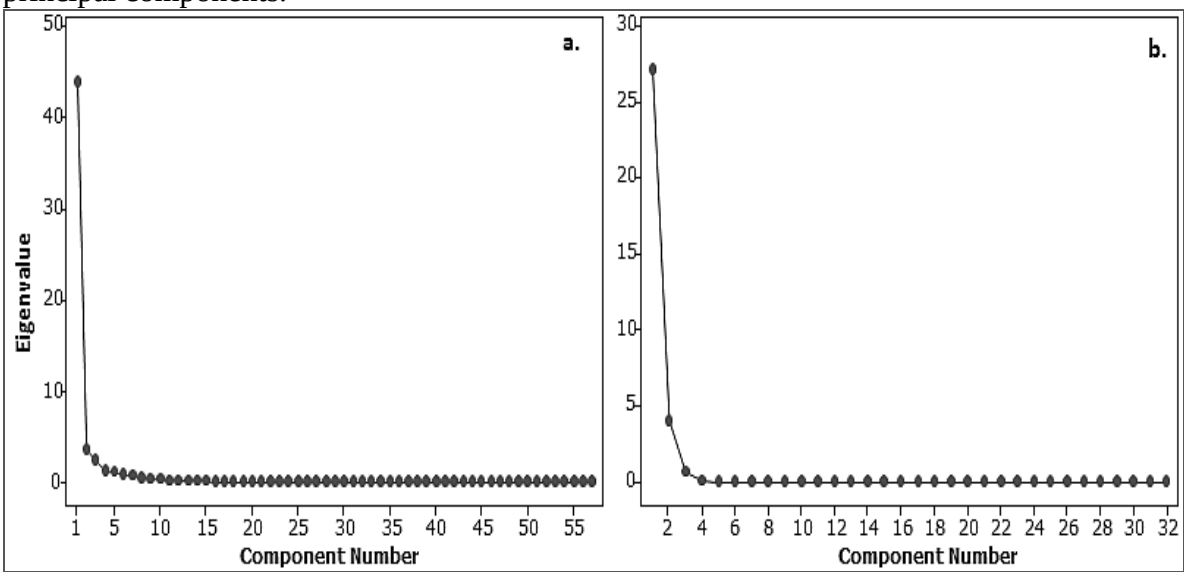
The cluster analysis implements hierarchical agglomerative clustering or partitioning of data into meaningful subgroups using the aforementioned resemblance matrix (Chapter 5) of Euclidean distance measure between samples (Clarke and Gorley, 2006). The selected cluster mode, which determines the algorithm for calculating the distances between clusters, for the present analysis is the single linkage option; here the new connection takes the maximum similarity of the individual links (P6). The results of hierarchical cluster analysis are best represented in the form of a tree diagram or a dendogram. It displays the groups formed by

clustering of observations (full sample set; x-axis) and their similarity levels (distance; y-axis). Dendograms of cluster analyses applied to the olefins-biomarker parameters and fatty acid data matrices comprising of the migration study samples, and corresponding variables (Appendix IV) are in Chapter 5.

The PC's are new, uncorrelated variables formed by linear combinations of the original variables (species); they account for the variation in the data. The maximum number, 'n', of principal components (PC1, PC2, PC3…, PCn) extracted for the analysis is equal to the number of variables. They are counts for each original species axis; for instance, PC1 is the sum of roughly equal contributions from each species and essentially orders the samples from low to high total abundance counts for subsequent PCs are distinguished at more subtle levels for samples with same total abundance (Clarke and Gorley, 2006). The first two PCs represent a plane of 'best fit', encompassing the maximum amount of variation in the sample points. Where the % variance (or proportion) explained by a third PC is small and dispensable, all points are projected perpendicularly on to the plane to obtain a 2D ordination plane which is seen to be almost seamless if the first two PCs account for a large proportion of the total variation.

The interpretation of the principal components could also be represented visually in the scree, or eigenvalue, plot as shown below. A steep curve, followed by a bend and then a straight line is the ideal trend. The components in the steep curve, just before the first point that starts the line trend are retained eigenvalues/PCs. For both migration olefins and acid data, it could be concluded that the first two-three principal components account for most of the total variability in data (given by the eigenvalues).

Scree (or eigenvalue) plots of a) olefins and biomarker parameter variables, and b) acid components of the correlation matrix displaying the component number versus the corresponding eigenvalue. The plot provides one method for determining the number of principal components.

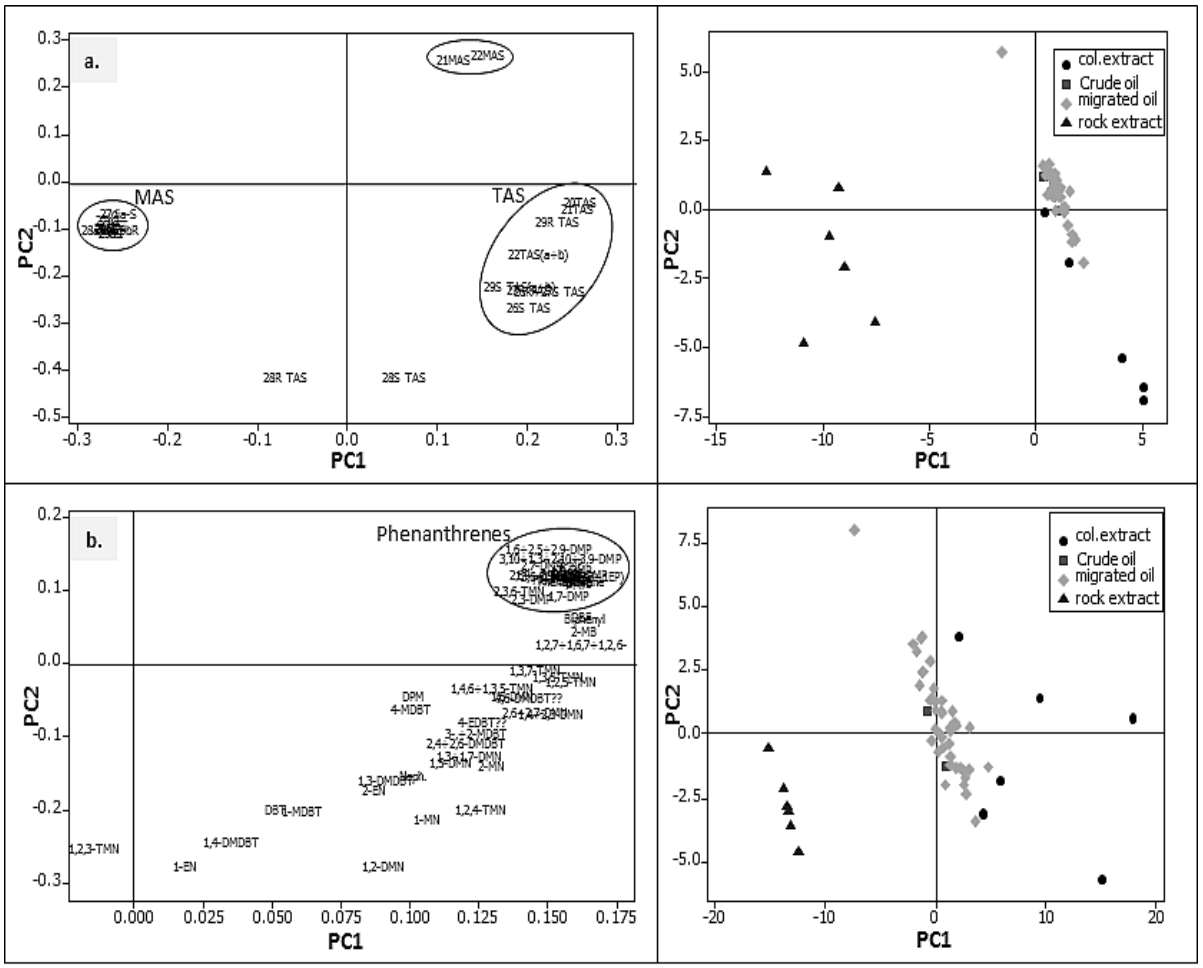


The PC % variation is the sum PC scores of all the components which are calculated using the eigenvectors. Eigenvectors are comprised of coefficients corresponding to each variable in the linear combinations that make up PC's, and are a measure of the relative weight of each variable in the component (Clarke and Gorley, 2006). The following expression simply illustrates how the PC1 score, for instance, is computed using the coefficients (eigenvectors) listed under the olefin-biomarker principal components (table in chapter 5):

Equation for calculating PC scores:

$$PC1 = (0.144 * H1) + (0.091 * H2) + (0.144 * H3) + (0.085 * H4) + \cdots + (-0.067 * P28)$$

Loadings and score plots from principal component analysis showing the relationships between the: a) aromatic steriod (MAS/TAS) hydrocarbons, and b) aromatic hydrocarbons and the first two principal components. All TAS, except 28R and 28S, have high positive, and low to zero negative loadings on PC1and PC2 respectively. All MAS (except 21MAS, 22MAS) show high negative loadings on PC1 and close to zero loading on PC2. Covarying biomarkers cluster together.



Appendix IV-f

BET Surface Area- Principles and Measurements

The BET model was used to determine the specific surface area of the sample. In order to describe and interpret the results, a number of the terms used need to be defined (e.g. Gregg and Sing, 1982) . These include:

- Adsorbent is the solid sample whose particles' surface areas were ultimately determined.

- Adsorbate is the term used to refer to the adsorptive material in its condensed gas (fluid) phase, and capable of being adsorbed. Nitrogen, helium and other inert pure gases may be used.

- Adsorptive may be defined as the gas phase in the sample tube and elsewhere.

- Adsorption was used here to denote the process in which adsorptive molecules transfer to and are accumulated in the interfacial layer (of the adsorbent). The inverse process- Desorption, refers to a situation where the amount of the adsorbed molecules declines.

- Specific surface area of a solid material is the entire surface of the sample that is in contact with the external environment. Expressed as square meters per gram (m^2/g) of dry sample, this factor has a strong relationship with pore size and the pore volume of the solid.

- Physisorption is a physical, irreversible process that brings the adsorptive in contact with the adsorbent surface. Also referred to as the van der Waals adsorption, it is the result of the attractive force acting between the exposed surface of a porous material and the molecules of a gas. Chemisorption is much more distinct due to its stronger bonding mechanism. It is irreversible at the adsorption temperature.

- Relative pressure is the ratio of the residual sample pressure (formed by non-adsorbed gas molecules) to the saturation vapour pressure.

- Saturation vapour pressure is considered to be the boiling pressure of the liquid gas, and varies with temperature.

- Free-space (or dead space) is the volume of the sample tube which is not filled with the sample. It is measured using a dosing inert gas such as Helium and calculated using the ideal gas model equations. Its measurement is vital to an accurate volumetric data output.

- Outgassing or degassing are terms interchangeably used here to mean the exposure of the surface of a solid to elevated temperature under vacuum in order to remove any physisorbed materials from the sample surface prior to adsorption measurements.

- Adsorption Isotherm is defined by the relationship between the amount of adsorbed gas and a range of relative gas pressures at a constant temperature (usually liquid N_2 @ 77K). The amount of adsorbed gas is reported in units of volume, mass or mole at standard temperature and pressure (STP). Conversely, the amount of gas removed, as gas pressure decreases, produces desorption isotherms.

Measurement Method for Adsorption Isotherm

The method used here, amongst many different others, for determining the amount of gas adsorbed is one of the methods which depend on the measurement of the amount of gas removed from the gas phase (Pierotti and Rouquerol, 1985). These are the gas volumetric methods. The BET instrument- Coulter SA 3100 Plus analyser employed in this analysis uses the static fully equilibrated volumetric method. With this method, discrete data points are obtained and are each equilibrated and readings recorded. Larger number of data points yield highly resolved results and vice versa for a rapid result in minutes. The volume of adsorbate gas retained by the adsorbent is derived from the measured pressure at each of these data points. The dosing gas, nitrogen in this case, has been calibrated to a constant volume. The free-space or dead space (e.g. Pierotti and Rouquerol, 1985) constitutes the initial unknown volume of the sample tube unoccupied by the sample. A known quantity of pure gas is used to determine this volume at the equilibrium pressure.

The isotherm volume data (y-axis) are calculated by subtracting the sample tube free-space from the total volume of gas dosed to the sample. An incremental set of data is formed from measured adsorbed gas volume, sample saturation pressure and relative pressure (x-axis) at each of the obtained data points.

BET Analysis Procedures

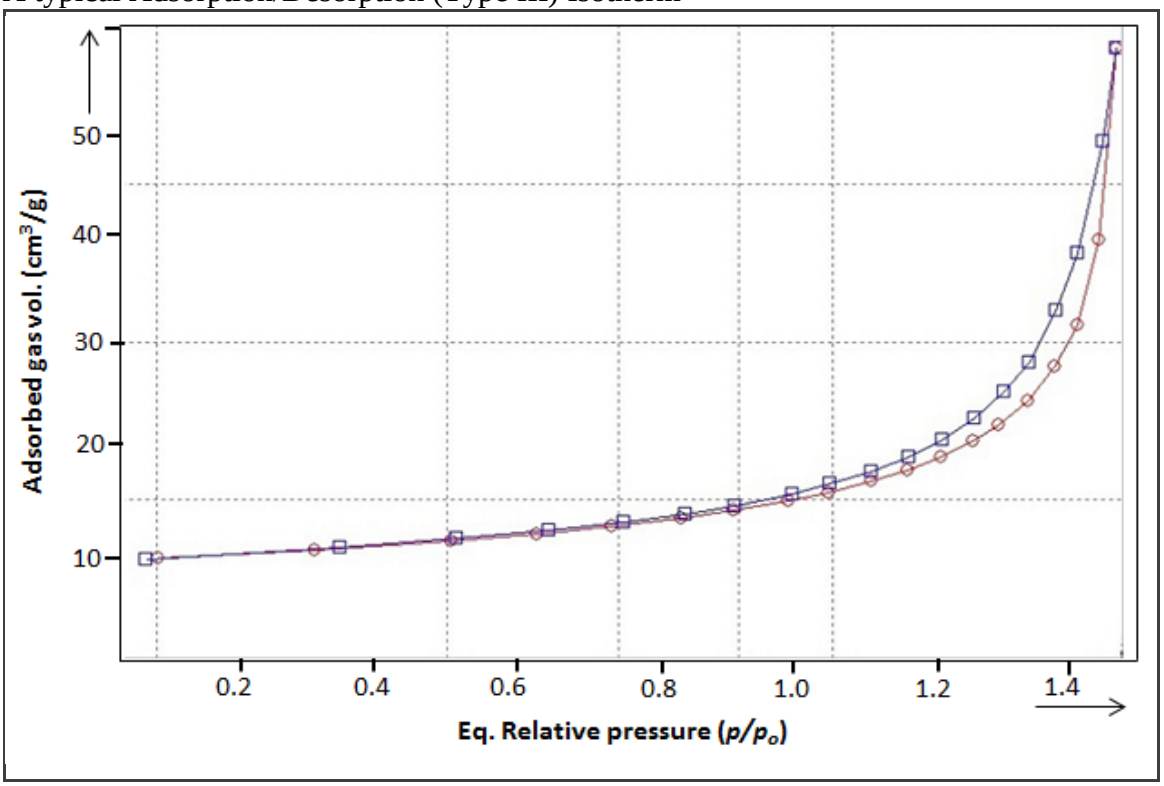
Prior to sample preparation, three clean, dry sample tube assemblies (without the cap) were first weighed on an analytical balance to at least 0.001g precision. Aliquots of samples, within the specified limits of the sample running instructions, were weighed and added to the sample tubes. The sample tubes and their contents were loaded onto the outgassing manifold for sample pre-treatment. Sample information and parameters for outgassing were logged on to instrument. Samples were first outgassed by removing any adsorbed water and organic vapours from the sample surfaces and tube. This was necessary to ensure accurate pore volume and specific surface area output. It involved flushing the adsorbents with pure inert gas and then exposing them to vacuum at elevated temperature of about 90^{o}C, for a minimum of 6 hours. The samples were then removed, capped and reweighed. These weights are critical in the determination of the surface areas, thus, standard precautions were taken to ensure accurate values. The weight of the sample (outgassed) was determined by weight differences.

The samples were then loaded on to the analyser, which was cautiously half-filled with liquid nitrogen. The analysis was started after the adsorbate was introduced in to the manifold. A pressure drop causes a recurrence of the gas dosing and this was continually measured until equilibrium is reached. The analysis for all three samples particles was completed within 48hours; the time taken to reach the equilibrium pressure and subsequently generate an isotherm is partly dependent on the nature of the sample and the number of data points to be acquired. Both free-space and isotherm measurements were automatically performed during the analysis. The analysis results, temporarily displayed on the screen, were recorded and could be stored for later use.

Data Presentation and Classification

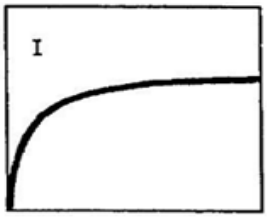
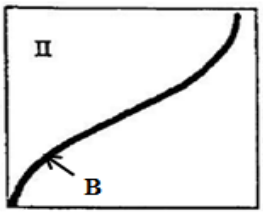
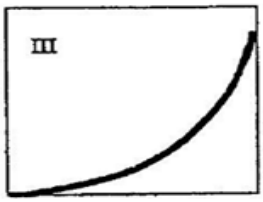
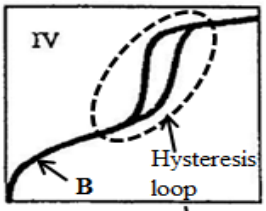
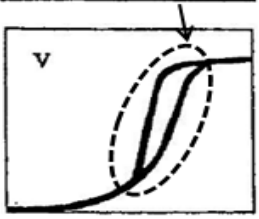
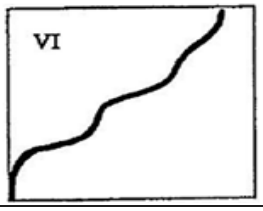
The quantity of adsorbed gas were measured and recorded in volumetric units at STP. It is expressed here in cubic centimetres per gram (cm^3/g) of outgassed sample. The adsorption isotherms were displayed graphically in the figure below; with the amount adsorbed (cm^3/g) values plotted on the y-axis against the independent equilibrium relative pressures (p/p_o).

A typical Adsorption/Desorption (Type III) Isotherm



Most physisorption isotherms are grouped into six types and includes the first five according to Brunauer et al. (1940) and a sixth type which was found later as part of the classification (e.g. Pierotti and Rouquerol, 1985, Lowell and Shields, 1991). Idealised representations of all six adsorption isotherms and a brief description of their occurrence are shown below. The adsorption isotherms and BET areas of the analysed samples were displayed on the instrument's analysis screen; the profiles of all three samples indicate a type II isotherm for the coarse (1-4mm) and a type I isotherm for the finest (<63µm) particles.

Types of van der Waals physisorption (Imaginary) isotherms, first described by Brunauer et al. (1940). The y- and x-axes units are amount of adsorbed gas (cm3/g) and relative pressures (p/po) respectively (adapted from Pierotti and Rouquerol (1985); Lowell and Shields (1991))

Adsorption isotherms		Brief description with examples
Type I		Concave to p/p_o axis; occurs in microporous solids with small external surface; at saturation point, n^a approaches limiting value as $p/p_o \rightarrow 1$, i.e. no amount of dosed gas can cause further adsorption. E.g. include Vulcan rubber, Si-Alumina, activated carbons, molecular sieve zeolites and certain porous oxides
Type II		Seen in non-porous or macroporous solids; depicts unlimited monolayer and multilayer adsorption; 'B' indicates the inflection point near the completion of first adsorbed monolayer and start of a multilayer adsorption. E.g. include Silica, Alumina, Zinc oxide (ZnO)
Type III		Convex to the p/p_o axis; uncommon; occurrence depends on adsorbate-adsorbate interactions; adsorbate-adsorbed layer interaction exceeds adsorbate-adsorbent surface interaction. Good example is N_2 on polyethylene
Type IV		Uncommon; characterised by hysteresis loops due to capillary condensation in mesopores and limiting uptake over high p/p_o range; initial part corresponds to type II isotherm, but occurs with porous adsorbents. An example is mesoporous industrial adsorbents
Type V		Uncommon; similar to type III with weak adsorbent-adsorbate interactions; associated with certain porous materials with pores in the range, 1.5-100nm.
Type VI		Stepwise multilayer adsorption on uniform, non-porous surface; step-sharpness depends on the system and temperature; step heights varies with monolayer capacity per adsorbed layer. Best example is Argon or Krypton on graphitized carbon blacks at liquid N_2 temperature.

Errors and limitations

Cumulative errors in measured doses of gas can result in a significant change which can reduce the accuracy of the adsorption measurements. The BET-N2 surface area can also be overestimated either as a result of capillary condensation at very low relative pressures or pores having constrictions less than ~0.5 nm (de Jonge and Mittelmeijer-Hazeleger, 1996).

The adsorptive nitrogen must be of high purity (＜99.9%) grade. The temperature of the liquid nitrogen must be regulated and monitored using the suitable vapour pressure manometer or other device. Its level in the Dewar must be maintained within a few millimetres and the sample probe immersed to a depth of, at least, 5cm below the liquid nitrogen level. Only a tiny portion of certain microporous solid total surface area is penetrable by nitrogen due to the molecular sieving effect of extremely small pores on the gas at 77K (Pierotti and Rouquerol, 1985).

All chosen condition for outgassing must be carefully controlled and monitored. The weight of the outgassed sample should be determined before or after the adsorption measurements (instrument manual).

Appendix III-a

Hopanoic Acid Data

Hopanoic acids (ppb)																																	
Sample Name	Basin	Region	Country	Sample ID	30-ab22S	30-ab22R	30-ba22S	30-ba22R	30-bb22S	30-bb22R	31-ab22S	31-ab22R	31-ba22S	31-ba22R	31-bb22S	31-bb22R	32-ab22S	32-ab22R	32-ba22S	32-ba22R	32-bb22S	32-bb22R	33-ab22S	33-ab22R	33-ba22S	33-ba22R	33-bb22S	33-bb22R	Tot.C30-HA	Tot.C31-HA	Tot.C32-HA	Tot.C33-HA	Tot.30-33HA
Adgo	Beaufort-Mackenzie		Canada	BMD01	677	320	198	539	496	472	0	465	277	708	241	2862	0	613	305	1620	290	5888	0	0	0	0	0	0	2702	4553	8716	0	15971
Adlartok	Beaufort-Mackenzie		Canada	BMD02	0	0	0	230	247	214	0	203	0	328	0	1081	0	534	200	0	0	2377	0	84	146	0	0	873	691	1611	3111	1102	6516
Kugpik	Beaufort-Mackenzie		Canada	BMD03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	179	184	0	0	389	0	0	0	0	0	0	1651	0	811	0	0	0	4046	0	0	0	0	0	1065	752	1651	4858	1065	8326
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	236	169	190	335	1683	783	0	368	0	295	137	2456	0	512	0	595	383	9522	0	324	346	223	357	3130	3396	3256	11012	4379	22043
ISS-0	Beaufort-Mackenzie		Canada	CAN06	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISS-4	Beaufort-Mackenzie		Canada	CAN08	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-aj	Kutei		Indonesia	KTM01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-IJ	Kutei		Indonesia	KTM02	0	0	0	0	0	0	0	155	97	172	0	77	0	114	0	40	0	270	0	0	0	0	0	0	0	500	425	0	925
Kut-v7	Kutei		Indonesia	KTM03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Asasa	Niger Delta	NE	Nigeria	NDE01	940	662	869	1725	1127	874	0	2975	2109	3734	1255	15051	1521	11893	1179	5200	4659	50012	1190	1664	1186	633	1143	8512	6197	25124	74465	14328	120115
Edop	Niger Delta	NE	Nigeria	NDE02	285	483	742	684	1017	752	0	1644	1090	1952	458	9604	554	8710	662	2181	3004	35431	439	962	690	512	526	4384	3963	14748	50542	7514	76767
Eku	Niger Delta	NE	Nigeria	NDE03	208	224	196	343	1250	845	216	545	434	783	252	3340	370	1520	273	841	733	12809	287	388	655	647	412	2857	3068	5570	16547	5248	30432
Etim	Niger Delta	NE	Nigeria	NDE04	0	350	162	783	794	567	496	948	525	1217	348	6144	589	5403	149	1561	1892	28469	501	475	746	384	438	3658	2656	9678	38062	6202	56597
Inanga	Niger Delta	NE	Nigeria	NDE05	202	122	176	296	159	199	239	357	296	363	0	649	103	624	102	364	87	1309	0	132	245	83	0	210	1154	1905	2589	671	6318
Ubit	Niger Delta	NE	Nigeria	NDE06	516	559	751	861	1159	711	517	1231	817	1501	246	3933	824	3239	695	1288	754	11814	687	776	746	523	402	2099	4557	8246	18614	5234	36651
Unam	Niger Delta	NE	Nigeria	NDE07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Yoho	Niger Delta	NE	Nigeria	NDE08	826	0	527	686	570	370	362	1645	1246	1585	0	4781	505	2878	626	1760	0	15141	400	1274	0	0	0	2624	2980	9620	20910	4298	37808
Dibi-6	Niger Delta	NW	Nigeria	NDW09	0	0	0	0	446	0	0	0	0	0	0	2334	0	744	0	0	0	2511	0	0	0	0	0	396	446	2334	3255	396	6431
Dibi-11	Niger Delta	NW	Nigeria	NDW10	153	333	271	567	515	387	0	899	508	839	0	1445	356	1577	320	818	0	2512	311	410	0	168	0	502	2226	3691	5584	1391	12893
Gbokoda	Niger Delta	NW	Nigeria	NDW11	892	979	2114	2290	1950	1107	1455	3347	2875	4361	0	11587	1143	4961	885	3575	877	19577	1194	0	2265	1320	725	4231	9331	23625	31018	9735	73708
Malu-27h	Niger Delta	NW	Nigeria	NDW12	409	369	666	642	659	357	463	1241	680	1213	198	2062	487	1834	240	934	0	2638	125	361	248	448	238	571	3103	5857	6133	1991	17084
Malu-28	Niger Delta	NW	Nigeria	NDW13	404	508	789	1185	1875	1307	725	1297	1154	2256	0	8980	309	3384	319	1628	1182	25182	616	739	909	656	361	3288	6069	14412	32004	6569	59054
Mer-12D	Niger Delta	NW	Nigeria	NDW14	0	313	0	346	0	1442	768	1357	929	1857	352	6000	789	2871	639	1261	511	13024	617	501	0	581	423	3186	2102	11263	19095	5308	37767
Meren-14	Niger Delta	NW	Nigeria	NDW15	1180	0	484	613	0	0	741	1329	1087	1676	0	986	373	1118	294	860	0	513	0	0	0	0	0	0	2277	5819	3159	0	11255
KC-W17	Niger Delta	Central	Nigeria	NDC16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KC-19t	Niger Delta	Central	Nigeria	NDC17	303	314	488	665	0	0	375	1050	652	1419	0	1726	439	1631	168	1015	0	1435	223	0	0	0	0	263	1771	5223	4689	486	12168
Oropouche	Ref. oil	Trinidad	Trinidad & Tob	TRO01	425	817	881	832	877	770	910	1371	768	1075	0	2421	749	1893	782	891	0	3989	579	1104	0	354	110	858	4602	6544	8304	3005	22455
Alba	Ref. oil	North Sea	UK	NSA02	0	0	0	0	0	0	0	0	0	0	0	2987	0	0	0	0	0	5280	0	0	0	0	0	1424	0	2987	5280	1424	9690
Andrew	Ref. oil	North Sea	UK	NSA03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NSA-74	Ref. oil	North Sea	n/a	NSA04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

IIIa*: n*-Acid Data

Normal & isoprenoid acids (ppm)																															
Sample Name	Basin	Region	Country	Sample ID	nC12	nC13	nC14	nC15	nC16	nC17	nC18	nC19	nC20	nC21	nC22	nC23	nC24	nC25	nC26	nC27	nC28	nC29	nC30	nC31	nC32	nC33	nC34	Pr-acid	Ph-acid	Est.Tn-A	Corr.Tn-A	SCA	LCA
Adgo	Beaufort-Mackenzie		Canada	BMD01	1	1.3	5.6	14.2	38.3	20	70.7	24.9	20.7	31.3	29.3	23.6	26	20.7	13.3	21	18.1	18.1	10.1	9.1	6.2	3.1	0.6	21.5	11.2	427.2	392	176	251
Adlartok	Beaufort-Mackenzie		Canada	BMD02	1.5	2.5	5.9	6.3	26.9	14.9	34.2	14.3	21.9	12.8	12.3	16.9	10.7	9	4.7	4.8	3.8	2.9	2.1	2.4	2.1	0	0	12.7	7.6	212.9	167	106	106
Kugpik	Beaufort-Mackenzie		Canada	BMD03	5.6	8	14.8	9.4	54.2	8	27.1	4.5	4.6	4.2	4.1	4.3	3.8	2.6	1.1	1.6	1.4	0.9	0.7	0.3	0.3	0	0	2.4	3.5	161.5	0	132	30
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	0	0	1.7	1.7	12.3	1	18.8	1.1	1.3	0.9	1.3	1.4	2.9	1.2	1.6	0.9	2.5	0.8	1.6	0	0.3	0	0	0	0.4	53.3	0	37	17
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	2.3	3.1	4.5	3.7	15.7	4.4	19.7	4.8	3.6	3.4	3.1	4	3.4	4	2.9	3.3	3	3.2	1.9	5	2.3	0	0	9.2	2	101.3	75	58	43
ISS-0	Beaufort-Mackenzie		Canada	CAN06	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISS-4	Beaufort-Mackenzie		Canada	CAN08	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-aj	Kutei		Indonesia	KTM01	0.3	0.8	4	2.3	19.3	1	19.3	0.4	0.3	0	0.2	0	0.1	0	0	0	0	0	0	0	0	0	0	2.5	2.6	48	16	47	1
Kut-lJ	Kutei		Indonesia	KTM02	0	0.5	7.6	9.3	69.8	20.7	98	1.9	6.8	1.4	3.1	1.3	2.1	1.2	1.1	1.1	1.7	1.1	1.2	1.4	0.9	0.5	0.1	4	6.1	232.8	51	208	25
Kut-v7	Kutei		Indonesia	KTM03	3.3	4.3	6.4	5.2	22.1	6.3	27.8	6.8	5	4.8	4.4	5.7	4.8	5.6	4.1	4.6	4.2	4.4	2.7	7.1	3.2	0	0	12.9	2.8	142.8	89	82	61
Asasa	Niger Delta	NE	Nigeria	NDE01	1.7	4.7	9.8	13.4	41.6	24.3	54.6	14.7	24.7	20.3	39.6	28.3	62.4	27.8	81.1	25.3	71.8	29	46.1	36.9	30.4	19.8	12.3	47.5	66.5	720.6	397	165	556
Edop	Niger Delta	NE	Nigeria	NDE02	3.3	2.9	6.3	6.6	18.5	9.8	23.1	6.8	11.8	10.6	20.1	15.8	31.3	16.4	36.1	16.3	39.5	16.5	25.8	20.7	13.5	7.6	4.4	17.8	35.4	363.7	272	77	286
Eku	Niger Delta	NE	Nigeria	NDE03	2	2.8	6.9	5.6	17.5	8.4	15.7	10.7	11.5	12.3	19.8	21.6	30.4	16.9	37.9	18.5	44.1	19.6	34	17.6	18.1	6	6.9	14	18.9	384.8	374	70	315
Etim	Niger Delta	NE	Nigeria	NDE04	2.4	2	10.1	8.9	48.3	13.9	82.3	10.4	17.7	13.9	28.2	19.7	44.6	19.4	50.7	17.9	52.9	16.5	37.4	17.7	21.2	9	8.6	19.8	24.1	553.7	546	178	375
Inanga	Niger Delta	NE	Nigeria	NDE05	0.2	0.1	2.3	1.7	11.7	1.4	7.4	2.1	3.6	3.6	5.1	4.7	6.4	4.8	6.5	5.6	12.2	6.2	16.8	5.7	8.7	3.7	3.5	7.3	11.4	124	110	27	97
Ubit	Niger Delta	NE	Nigeria	NDE06	3.7	5.2	9.2	12.6	19.7	21.8	21.3	14.9	22.2	25.4	37.3	43.8	52.1	31.2	45.9	23.3	37.3	19.5	21.6	16.1	10.5	4.3	4.3	38.7	49.4	503.2	495	108	395
Unam	Niger Delta	NE	Nigeria	NDE07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Yoho	Niger Delta	NE	Nigeria	NDE08	0.8	2.3	8	8.8	21.9	13.9	23.6	13.7	25.1	22.7	45.8	32.2	64.5	35.5	89.9	34.8	97.1	28.6	57.7	22.6	32.7	10.3	12.5	21.6	38.8	705	527	93	612
Dibi-6	Niger Delta	NW	Nigeria	NDW09	4971.5	6.8	1184.3	6.6	232.3	6.3	67.6	1.8	7.1	2.7	4.6	3.8	6.7	3.9	6	3.7	9.8	3.2	7.8	1.9	4	1	1.4	6	10.7	6544.8	6510	6477	68
Dibi-11	Niger Delta	NW	Nigeria	NDW10	95.7	4.1	54	6.7	37.2	8.7	48	7.4	10.3	9.2	12.2	10.1	13.6	8.7	12.9	7.4	12.8	5.6	10.5	3.8	5.9	4.1	3.1	18.9	21.2	392	380	262	130
Gbokoda	Niger Delta	NW	Nigeria	NDW11	680.6	4.9	361.1	8.2	99.4	12.9	41.2	4.6	8.3	4.9	5.6	5.2	4.8	3.2	7.8	6.8	5.3	6	4	4.6	2.3	0	0	14.7	46.9	1281.7	1204	1213	69
Malu-27h	Niger Delta	NW	Nigeria	NDW12	1.5	2.3	6	5.8	12.3	5.8	10.2	6.1	9.9	10.4	14.8	14.2	23.1	15.8	32	20.1	54.2	21.6	55.9	15.7	33.7	9.9	13.5	19.3	25.2	394.8	383	50	345
Malu-28	Niger Delta	NW	Nigeria	NDW13	1.7	2.3	13.5	11.1	56	12.7	41	6.3	10.9	6.6	14.4	9.1	18.7	6.8	11.7	4.8	12.2	4.6	11.7	7.3	11.1	6.8	4.5	36.4	19.3	285.8	258	145	141
Mer-12D	Niger Delta	NW	Nigeria	NDW14	1.5	1.3	4.3	3.7	13	3.6	15.9	4.4	3.9	3.6	3.8	3.6	4.4	3.5	5.8	4.6	10.1	6.2	11.5	13.3	10.7	10	7.3	5	6.9	150	144	48	102
Meren-14	Niger Delta	NW	Nigeria	NDW15	2.2	2.8	9.2	8.2	28.2	9.6	19.8	7.2	10.2	9	13.2	12.4	18.8	14.9	26.2	20.2	48	22.5	49.2	16.8	29.8	10.7	11.1	22.5	32.6	400.2	29	87	313
KC-W17	Niger Delta	Central	Nigeria	NDC16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KC-19t	Niger Delta	Central	Nigeria	NDC17	3	5.5	13.8	11.8	49.1	15.6	64.5	13.2	20.4	16.9	27.4	21.2	34.7	20.9	41.4	22.2	60.5	20.7	52.5	15.8	37.4	11.5	21.8	25.4	38.3	601.8	531	177	425
Oropouche	Ref. oil	Trinidad	Trinidad & Tobego	TRO01	11.4	1.8	9.9	6.3	22.9	5.8	16.4	4.7	6.2	5.3	6.9	6.5	7.9	5.1	7.7	4.8	7.2	3.7	5.5	6.6	3	4.1	1.4	14.6	14.5	161.1	126	79	82
Alba	Ref. oil	North Sea	UK	NSA02	3.6	8.7	9.1	14.9	38.9	4	59.3	2.5	4.3	2.6	3.2	3.2	3	1.3	0	0.8	2.2	1.4	0.8	2.9	1	0.1	0.1	6.9	1.4	167.9	139	141	27
Andrew	Ref. oil	North Sea	UK	NSA03	0.3	0.6	2.4	1.9	7.8	1.6	4.5	0.6	0.6	0.4	0.5	0.3	0.5	0.3	0.3	0.2	0.2	0.1	0.1	0	0	0	0	0.6	0.9	23.2	16	20	4
NSA-74	Ref. oil	North Sea	n/a	NSA04	0.7	0.9	3.2	2.3	15.2	1.7	15.5	0.5	0.8	0.5	0.5	0.4	0.5	0.3	0.1	0.2	0.2	0	0	0	0	0	0	0.8	0.8	43.5	0	40	4
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	0.2	0.2	1	0.8	4.3	0.9	3.3	0.2	0.7	0.5	0.3	0.4	0.3	0.2	0.2	0.2	0.4	0.2	0	0.1	0	0	0	0.6	0.6	14.4	0	11	4

IIIa: *n*-Alkene Data

Normal alkenes (ppb)																					
Sample Name	Basin	Region	Country	Sample ID	n-C12	n-C13	n-C14	n-C15	n-C16	n-C17	n-C18	n-C19	n-C20	n-C21	n-C22	n-C23	n-C24	n-C25	n-C26	n-C27	?Squalene	Tot.n-olefins
Adgo	Beaufort-Mackenzie		Canada	BMD01	0	0	77	19	37	0	26	61	71	0	16	0	0	0	0	0	508	306
Adlartok	Beaufort-Mackenzie		Canada	BMD02	0	0	10	11	116	87	223	64	205	0	159	0	127	0	67	0	486	1070
Kugpik	Beaufort-Mackenzie		Canada	BMD03	0	0	75	38	188	147	188	74	74	72	93	66	25	0	0	0	1422	1040
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	0	9	230	76	218	230	313	170	248	88	204	0	0	0	0	0	244	1784
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	0	28	230	95	151	115	108	64	74	0	35	0	0	0	0	0	198	899
ISS-0	Beaufort-Mackenzie		Canada	CAN06	0	0	1085	193	1688	845	582	450	240	303	154	457	0	1107	0	0	0	7106
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	0	7362	0	2197	2813	0	0	688	0	0	0	956	497	0	0	0	14512
ISS-4	Beaufort-Mackenzie		Canada	CAN08	0	0	1003	231	690	0	0	0	0	0	169	247	0	0	0	0	0	2340
Kut-aj	Kutei		Indonesia	KTM01	0	0	143	28	777	115	1345	46	868	0	360	0	107	0	23	0	173	3812
Kut-IJ	Kutei		Indonesia	KTM02	0	0	1159	46	478	132	768	59	460	0	399	17	383	12	275	0	381	4188
Kut-v7	Kutei		Indonesia	KTM03	0	0	8	6	50	23	84	54	56	0	23	0	0	0	0	0	178	303
Asasa	Niger Delta	NE	Nigeria	NDE01	0	0	37	0	91	38	111	21	61	21	21	0	0	0	0	0	756	401
Edop	Niger Delta	NE	Nigeria	NDE02	113	0	2256	615	2080	426	4183	1094	2512	862	743	979	357	686	0	386	0	17292
Eku	Niger Delta	NE	Nigeria	NDE03	0	0	325	0	419	122	1256	375	1603	783	710	573	174	409	115	354	223	7219
Etim	Niger Delta	NE	Nigeria	NDE04	0	0	62	0	615	157	241	531	1756	626	554	573	206	293	0	205	172	5819
Inanga	Niger Delta	NE	Nigeria	NDE05	0	0	826	0	1656	0	2370	753	1702	0	459	8504	0	472	0	323	1115	17066
Ubit	Niger Delta	NE	Nigeria	NDE06	1079	0	4844	0	0	0	3102	8014	0	4465	0	0	7873	806	724	1526	0	32434
Unam	Niger Delta	NE	Nigeria	NDE07	0	0	2396	0	2187	265	2664	836	1357	0	243	8243	116	327	0	0	333	18635
Yoho	Niger Delta	NE	Nigeria	NDE08	0	17	142	0	116	19	87	14	56	0	31	0	0	0	0	0	875	482
Dibi-6	Niger Delta	NW	Nigeria	NDW09	0	0	198	0	915	232	3254	654	2682	812	722	1300	419	376	0	402	593	11966
Dibi-11	Niger Delta	NW	Nigeria	NDW10	0	0	724	0	811	178	1400	411	1317	384	621	343	346	183	151	141	0	7010
Gbokoda	Niger Delta	NW	Nigeria	NDW11	0	0	9	4	108	0	186	55	74	0	32	0	0	0	0	0	191	467
Malu-27h	Niger Delta	NW	Nigeria	NDW12	0	320	2198	342	910	0	620	628	377	0	0	0	0	0	0	0	0	5395
Malu-28	Niger Delta	NW	Nigeria	NDW13	85	0	5965	220	2956	319	3057	447	1341	538	350	256	157	199	0	222	2768	16112
Mer-12D	Niger Delta	NW	Nigeria	NDW14	955	0	13295	0	7705	776	6284	943	2026	0	546	3106	197	596	0	0	4269	36429
Meren-14	Niger Delta	NW	Nigeria	NDW15	74	0	3280	0	2335	294	308	405	1457	0	403	1713	187	367	0	184	487	11008
KC-W17	Niger Delta	Central	Nigeria	NDC16	247	0	7455	3255	24314	705	8114	1939	3807	1240	1554	1281	442	674	495	659	704	56181
KC-19t	Niger Delta	Central	Nigeria	NDC17	244	0	1467	285	1166	288	3072	0	5196	0	5924	0	5137	0	3576	0	0	26356
Oropouche	Ref. oil	Trinidad	Trinidad & Tobego	TRO01	524	0	1628	467	1209	0	692	0	343	0	0	0	0	0	0	0	64	4862
Alba	Ref. oil	North Sea	UK	NSA02	296	0	868437	0	511516	328	709	364	685	0	240	0	0	0	0	0	77	2575
Andrew	Ref. oil	North Sea	UK	NSA03	0	0	457	383	356	354	256	181	287	145	96	0	0	0	0	0	130	2515
NSA-74	Ref. oil	North Sea	n/a	NSA04	0	0	32	0	164	110	85	107	146	78	43	0	0	0	27	0	39	790
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	0	0	147	110	277	239	215	139	274	57	75	0	102	0	0	0	336	1634

IIIa: Triterpene Data

					Hop-17,21-enes (ppb)												Oleanenes (ppb)					
Sample Name	Basin	Region	Country	Sample ID	C30	C31 22S	C31 22R	C32 22S	C32 22R	C33 22S	C33 22R	C34 22S	C34 22R	C35 22S	C35 22R	Sum C30-C35	Ol-13,18-ene	Ol-12-ene	Ol-18-ene	Urs12-ene	18α-Ol-12-ene	Ol-+Urs-ene
Adgo	Beaufort-Mackenzie		Canada	BMD01	1176	0	328	0	218	0	102	45	70	0	43	1983	0	0	0	0	0	0
Adlartok	Beaufort-Mackenzie		Canada	BMD02	673	0	383	0	145	0	69	0	30	0	16	1316	0	0	1462	0	0	1462
Kugpik	Beaufort-Mackenzie		Canada	BMD03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	98	52	64	21	33	0	36	0	0	0	0	303	0	0	350	0	0	350
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	2100	36	641	0	165	0	76	0	43	0	8	3069	0	0	1647	0	0	1647
ISS-0	Beaufort-Mackenzie		Canada	CAN06	853	1502	1239	495	487	267	211	208	129	86	77	5555	5684	3154	6637	20612	6534	42621
ISS-3	Beaufort-Mackenzie		Canada	CAN07	312	105	82	20	7	0	0	0	0	0	0	526	1197	635	603	4051	1314	7800
ISS-4	Beaufort-Mackenzie		Canada	CAN08	2521	3291	3883	863	986	409	494	317	334	265	255	13617	9958	3973	5314	36823	8465	64533
Kut-aj	Kutei		Indonesia	KTM01	6	0	5	0	0	0	0	0	0	0	0	11	0	0	96	0	0	96
Kut-IJ	Kutei		Indonesia	KTM02	48	14	33	0	15	0	0	0	0	0	0	111	0	0	958	0	0	958
Kut-v7	Kutei		Indonesia	KTM03	16	0	16	0	8	0	0	0	0	0	0	40	0	0	287	0	0	287
Asasa	Niger Delta	NE	Nigeria	NDE01	796	329	709	76	267	0	142	0	70	0	28	2417	0	0	4243	0	0	4243
Edop	Niger Delta	NE	Nigeria	NDE02	0	292	187	163	115	74	43	48	21	21	0	964	0	0	5881	9375	1011	16267
Eku	Niger Delta	NE	Nigeria	NDE03	0	347	0	162	0	96	0	58	0	30	0	694	880	9657	5313	9724	1203	26777
Etim	Niger Delta	NE	Nigeria	NDE04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3758	226	20	4004
Inanga	Niger Delta	NE	Nigeria	NDE05	0	101	39	54	0	34	0	14	0	0	0	241	209	563	3628	6289	0	10690
Ubit	Niger Delta	NE	Nigeria	NDE06	0	84	0	58	0	49	0	0	0	0	0	191	0	0	16368	26795	0	43163
Unam	Niger Delta	NE	Nigeria	NDE07	0	147	74	91	53	42	0	39	0	0	0	445	277	2008	8519	12360	1170	24334
Yoho	Niger Delta	NE	Nigeria	NDE08	2153	363	1629	43	520	0	220	36	101	0	34	5101	0	0	7083	0	0	7083
Dibi-6	Niger Delta	NW	Nigeria	NDW09	0	0	0	0	0	0	0	0	0	0	0	0	0	0	812	344	44	1200
Dibi-11	Niger Delta	NW	Nigeria	NDW10	0	22	0	18	0	12	0	0	0	0	0	52	62	71	238	339	37	747
Gbokoda	Niger Delta	NW	Nigeria	NDW11	264	412	490	120	232	37	94	20	59	0	32	1761	0	0	4112	0	0	4112
Malu-27h	Niger Delta	NW	Nigeria	NDW12	694	1955	1508	954	917	426	320	264	181	127	89	7434	0	0	30838	1607	0	32445
Malu-28	Niger Delta	NW	Nigeria	NDW13	231	992	891	480	503	268	175	218	133	128	110	4128	1568	8847	11382	23669	2232	47699
Mer-12D	Niger Delta	NW	Nigeria	NDW14	0	448	56	287	0	139	0	88	0	66	0	1084	1046	22274	4977	10289	1306	39892
Meren-14	Niger Delta	NW	Nigeria	NDW15	0	58	22	33	22	19	0	0	0	0	0	154	162	427	2963	4284	455	8292
KC-W17	Niger Delta	Central	Nigeria	NDC16	0	420	307	182	144	95	64	55	32	19	14	1333	0	0	2943	5570	0	8513
KC-19t	Niger Delta	Central	Nigeria	NDC17	1253	2561	881	999	440	439	107	185	71	87	22	7044	0	0	13000	1975	0	14975
Oropouche	Ref. oil	Trinidad	Trinidad & Tobego	TRO01	2087	1605	1147	436	376	181	111	106	58	54	22	6182	0	0	1142	2929	0	4071
Alba	Ref. oil	North Sea	UK	NSA02	249	808	534	762	742	588	488	423	348	455	347	5744	0	0	411	142	0	554
Andrew	Ref. oil	North Sea	UK	NSA03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NSA-74	Ref. oil	North Sea	n/a	NSA04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	10	42	38	38	37	39	30	25	19	12	6	294	0	0	0	0	0	0

IIIa: Diasterene Data

Diasterenes (ppb)																				
					Diaster-13,17-enes									Me-diasterenes (4β-Me-10α-)							
Sample Name	Basin	Region	Country	Sample ID	10b20S	10a20S	10b20R	10a20R	24Me10aS	24Me10aR	24Et-10aS	24Et-10bR	24Et-10aR	C28-20S	C28-20R	C29-20S	0S+C29R-m	C30*x	C30-20R	C30*y	Tot. Diasterenes
Adgo	Beaufort-Mackenzie		Canada	BMD01	69	432	241	1289	916	985	3448	3256	19021	109	187	181	604	633	211	666	32247
Adlartok	Beaufort-Mackenzie		Canada	BMD02	233	1036	183	1137	2071	2672	13699	2990	16824	158	130	361	654	320	237	497	43202
Kugpik	Beaufort-Mackenzie		Canada	BMD03	1	5	2	8	8	2	10	8	10	1	1	1	2	1	1	1	62
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	170	727	105	637	1178	547	2547	499	1627	82	48	113	217	70	107	81	8755
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	245	1130	207	1197	2112	1798	9545	1760	8806	151	138	298	478	164	269	319	28617
ISS-0	Beaufort-Mackenzie		Canada	CAN06	1544	6193	722	4540	11407	12828	46763	8188	32281	754	754	2249	3310	498	1287	1115	134432
ISS-3	Beaufort-Mackenzie		Canada	CAN07	415	2028	453	740	3146	1646	8278	1252	4840	186	121	236	130	144	172	126	23913
ISS-4	Beaufort-Mackenzie		Canada	CAN08	2587	11371	982	10583	21414	19389	81093	16168	68163	1636	1903	3802	3907	1108	2882	3205	250192
Kut-aj	Kutei		Indonesia	KTM01	7	22	4	20	37	31	159	22	118	2	2	8	13	6	3	4	457
Kut-IJ	Kutei		Indonesia	KTM02	31	122	34	136	237	181	969	128	716	16	18	36	98	37	23	30	2810
Kut-v7	Kutei		Indonesia	KTM03	42	112	23	107	166	165	767	113	567	13	10	22	33	11	10	15	2176
Asasa	Niger Delta	NE	Nigeria	NDE01	113	546	90	583	461	211	1234	227	793	51	50	85	156	32	91	87	4811
Edop	Niger Delta	NE	Nigeria	NDE02	40	141	70	0	155	96	315	0	82	0	0	0	0	0	0	0	898
Eku	Niger Delta	NE	Nigeria	NDE03	34	97	105	0	196	91	468	60	188	0	34	31	61	44	0	0	1410
Etim	Niger Delta	NE	Nigeria	NDE04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Inanga	Niger Delta	NE	Nigeria	NDE05	36	112	30	60	113	125	421	90	222	36	0	0	40	35	57	0	1377
Ubit	Niger Delta	NE	Nigeria	NDE06	33	125	79	0	115	117	605	94	126	0	0	0	0	0	0	0	1295
Unam	Niger Delta	NE	Nigeria	NDE07	39	85	45	30	135	79	322	53	116	0	0	0	0	0	0	0	904
Yoho	Niger Delta	NE	Nigeria	NDE08	69	341	59	394	363	177	1112	214	787	36	37	57	145	33	72	78	3976
Dibi-6	Niger Delta	NW	Nigeria	NDW09	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Dibi-11	Niger Delta	NW	Nigeria	NDW10	0	15	14	0	21	14	44	0	29	0	0	0	0	0	0	0	137
Gbokoda	Niger Delta	NW	Nigeria	NDW11	78	331	53	300	252	138	766	135	463	34	32	42	86	24	49	41	2826
Malu-27h	Niger Delta	NW	Nigeria	NDW12	271	1265	275	1006	1336	1115	4880	745	3079	129	169	341	476	99	320	230	15735
Malu-28	Niger Delta	NW	Nigeria	NDW13	166	653	239	470	725	468	2160	520	1317	61	124	140	331	115	201	59	7749
Mer-12D	Niger Delta	NW	Nigeria	NDW14	18	27	254	0	0	58	113	43	449	35	34	31	230	60	0	0	1350
Meren-14	Niger Delta	NW	Nigeria	NDW15	22	58	0	0	58	49	155	50	71	0	0	0	0	0	0	0	463
KC-W17	Niger Delta	Central	Nigeria	NDC16	79	322	54	40	346	157	751	36	279	38	0	67	109	0	0	0	2279
KC-19t	Niger Delta	Central	Nigeria	NDC17	299	1189	468	388	1278	820	3160	414	1527	79	86	214	495	98	111	49	10675
Oropouche	Ref. oil	Trinidad	Trinidad & Tobego	TRO01	260	1142	480	917	1269	483	2213	354	1611	87	128	193	570	158	118	105	10087
Alba	Ref. oil	North Sea	UK	NSA02	1617	6567	1070	5321	6088	2813	12416	2122	6632	1543	1556	2223	3518	1363	2467	1180	58495
Andrew	Ref. oil	North Sea	UK	NSA03	170	730	81	590	607	254	1303	218	725	130	155	192	247	79	178	74	5735
NSA-74	Ref. oil	North Sea	n/a	NSA04	21	105	11	29	90	26	153	26	114	25	18	20	13	9	35	8	703
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	218	910	129	520	915	350	1642	167	753	191	138	242	124	103	204	82	6688

Appendix III-b

n-Alkane and Isoprenoid Alkane Data

Normal and Isoprenoid Alkanes (ppm)																																				
Sample Name	Basin	Region	Country	Sample ID	n-C9	n-C10	n-C11	n-C12	n-C13	n-C14	n-C15	n-C16	n-C17	Pristane	n-C18	Phytane	n-C19	n-C20	n-C21	n-C22	n-C23	n-C24	n-C25	n-C26	n-C27	n-C28	n-C29	n-C30	n-C31	n-C32	n-C33	n-C34	n-C35	nC36	Tot.*n*-alkanes
Adgo	Beaufort-Mackenzie		Canada	BMD01	168	70	2286	850	1053	423	830	249	130	108	289	300	147	203	11	100	10	6	3	0	0	0	0	0	0	0	0	0	0	0	0	6828
Adlartok	Beaufort-Mackenzie		Canada	BMD02	305	1227	1695	3589	9607	4544	3547	3517	3387	8203	1992	2487	1548	1264	744	594	444	326	248	272	162	61	81	34	38	0	0	0	0	0	39226
Kugpik	Beaufort-Mackenzie		Canada	BMD03	4841	7698	8994	10621	12610	12364	13194	11431	10792	6789	9536	4081	7802	7720	6804	6408	5759	5133	4146	3361	2078	1372	768	484	315	139	88	42	12	0	154512
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	709	1723	1578	2473	3681	2933	3326	2954	2811	2980	2127	1825	1967	1977	1847	1703	1527	1455	1211	1289	780	584	519	492	404	250	197	0	0	0	40517
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	621	2113	7691	8679	12876	9779	9330	7765	6791	4289	5587	3926	4071	2518	1412	672	321	171	80	44	47	32	23	18	13	0	0	0	0	0	80654
ISS-0	Beaufort-Mackenzie		Canada	CAN06	0	123	856	2951	6426	8227	11655	11790	10781	15512	9459	3756	8738	7964	6818	5997	5323	4199	3662	2823	2441	1496	1450	816	1397	379	322	113	0	0	116206
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	575	4126	4416	10869	10261	7243	2846	1247	5427	100	1069	187	223	122	56	80	24	42	107	28	0	0	0	0	0	0	0	0	0	42552
ISS-4	Beaufort-Mackenzie		Canada	CAN08	85	434	845	1832	3209	2740	3677	1590	1566	11795	226	2973	1080	1248	889	772	752	564	590	540	459	242	287	244	931	338	92	0	0	0	25232
Kut-aj	Kutei		Indonesia	KTM01	102	5091	25267	44933	10408	43961	32196	20280	13450	19124	8022	1705	4761	2525	1363	759	442	260	158	22	0	0	0	0	0	0	0	0	0	0	214000
Kut-IJ	Kutei		Indonesia	KTM02	0	0	405	2134	8739	25400	78537	78382	47716	11423	5755	1104	1652	1427	1199	1069	855	724	542	554	321	224	158	120	0	0	0	0	0	0	255913
Kut-v7	Kutei		Indonesia	KTM03	226	3247	8376	13818	13728	23400	25421	24676	24437	27250	18855	4480	16582	14453	12242	9920	7393	4966	3117	1936	1145	597	359	176	0	0	0	0	0	0	229070
Asasa	Niger Delta	NE	Nigeria	NDE01	1578	2010	3006	4527	7699	6440	7109	5864	5328	8784	4382	3059	4040	3670	3376	2936	2817	2528	2228	2041	1795	1422	1361	1078	1448	623	657	0	0	0	79963
Edop	Niger Delta	NE	Nigeria	NDE02	1029	3300	3824	4772	5717	6731	7589	6382	5502	8297	5108	2979	4600	4298	4251	4123	4088	3908	3881	3366	3282	2846	2996	2256	2146	1152	935	574	297	131	99084
Eku	Niger Delta	NE	Nigeria	NDE03	1705	3917	3631	4230	4470	5451	6805	5856	5500	8353	4991	2771	4824	4706	4754	4696	4850	4667	4706	4311	4200	3477	3460	2570	2273	1181	990	507	275	110	103113
Etim	Niger Delta	NE	Nigeria	NDE04	2852	6444	6885	7364	7117	6977	7016	6042	5522	7039	4826	2612	4483	4279	4123	3882	3766	3537	3530	3189	3177	2866	2877	2174	2127	1316	1101	544	386	200	108602
Inanga	Niger Delta	NE	Nigeria	NDE05	3269	6422	6968	7071	6916	6802	7083	6040	5662	8141	5257	2149	4959	4925	4863	4878	4885	4802	4788	4334	4288	3673	3603	2626	2521	1451	1333	580	436	0	120435
Ubit	Niger Delta	NE	Nigeria	NDE06	362	1694	1575	3073	4404	5629	6877	6029	5626	7720	5023	2853	4786	4593	4604	4416	4397	4153	4184	3516	3465	2918	2815	2049	1870	1146	946	437	315	14	90916
Unam	Niger Delta	NE	Nigeria	NDE07	2125	4310	4562	5121	5152	5480	6234	5418	5195	7144	4468	2605	4214	4004	4075	3912	3896	3783	3868	3413	3537	3277	3606	2800	2716	1620	1378	772	471	233	99640
Yoho	Niger Delta	NE	Nigeria	NDE08	6197	8057	8117	8975	11864	10194	10584	9354	8760	10317	7293	2407	6869	6437	6024	5602	5282	4832	4484	4050	3646	2957	2890	2013	2649	1123	1075	426	284	0	150038
Dibi-6	Niger Delta	NW	Nigeria	NDW09	631	2916	4606	5392	5486	5565	5726	5212	5055	2708	4509	1297	4329	4140	4000	3664	3494	3200	3032	2587	2387	1906	1619	1125	862	540	356	180	101	0	82620
Dibi-11	Niger Delta	NW	Nigeria	NDW10	3924	9544	11184	11461	11303	11033	11222	10476	9513	3804	8150	1996	8007	7604	7342	6985	6844	6397	6137	5398	5177	4180	3697	2731	2154	1406	993	541	342	0	173745
Gbokoda	Niger Delta	NW	Nigeria	NDW11	167	252	196	580	2844	743	425	103	349	5829	153	3328	219	27	392	84	110	196	258	85	219	137	78	233	659	701	317	111	0	0	9638
Malu-27h	Niger Delta	NW	Nigeria	NDW12	11481	15521	15895	15564	16719	14274	13816	12164	11125	5317	9869	1963	9090	8570	8131	7697	7384	6865	6614	5988	5542	4443	3937	2814	2743	1585	1131	748	372	268	220350
Malu-28	Niger Delta	NW	Nigeria	NDW13	4891	8895	8597	7130	6378	5716	5785	4634	4251	3309	3644	1533	3464	3339	3286	3139	3194	3046	3097	2769	2801	2273	2163	1728	1405	834	623	311	190	111	97694
Mer-12D	Niger Delta	NW	Nigeria	NDW14	493	1451	1880	1929	2042	2308	2003	1805	1307	3306	1105	1873	1016	968	1017	810	827	833	885	752	732	605	852	680	478	298	159	137	115	0	27487
Meren-14	Niger Delta	NW	Nigeria	NDW15	5502	11452	13047	14157	13333	12765	12396	10240	8946	4805	7632	1896	6900	6285	5968	5517	5286	4972	4652	4094	3923	3175	2887	2100	1655	1029	771	465	264	0	169413
KC-W17	Niger Delta	Central	Nigeria	NDC16	171	661	1461	2340	6878	17458	30271	33080	32202	32221	28715	10081	24137	20275	16997	14661	12625	10562	8741	6761	5486	3939	3134	1850	1517	723	486	229	125	0	285485
KC-19t	Niger Delta	Central	Nigeria	NDC17	5566	11753	16722	19434	24196	19917	19478	16450	14805	11697	12150	3026	10838	9525	8553	7464	6686	5745	5149	4463	3916	3010	2648	1913	2128	1026	751	316	0	0	234602
Oropouche	Ref. oil	Trinidad	Trinidad &	TRO01	4529	7069	7862	9454	13494	9894	9325	9055	8339	3816	7366	2395	6964	6725	6882	5816	5322	4989	4540	4096	3528	3074	2459	1955	1744	1090	602	394	244	0	146811
Alba	Ref. oil	North Sea	UK	NSA02	0	251	21	39	236	181	280	100	57	1130	179	1124	320	111	47	5	5	14	147	151	4	192	68	145	0	341	161	181	0	0	3236
Andrew	Ref. oil	North Sea	UK	NSA03	3141	11448	15748	16583	21476	15122	13584	11795	10578	5577	8518	4123	7585	7009	5869	5163	4483	4129	3575	3182	2472	2068	1686	1323	1044	690	323	0	0	0	178594
NSA-74	Ref. oil	North Sea	n/a	NSA04	4320	11098	13792	14950	19811	14755	13143	12109	10420	5660	8960	4372	7586	7361	6041	5364	4737	4370	4013	3357	2600	2272	1720	1433	1137	776	374	346	173	0	177018
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	7101	14764	15644	15581	18439	12988	12388	9533	8374	6357	6680	4147	5769	5395	4373	3845	153	3153	2751	2442	1948	1667	1336	1201	1079	734	508	530	329	0	158705

IIIb: Triterpane Data

Terpanes (ppm)																													
Sample Name	Basin	Region	Country	Sample ID	C27Ts	C27Tm	28,30-BNH	29, 25NH17a	C29,ab30NH	C29Ts	C30*17a-DH	C29,ba-NH	C30-OI	C30H	C30baH	C31-22S	C31-22R	C31-Gam	C31ba22S+R	C32-22S	C32-22R	C32ba22S+R	C33-22S	C33-22R	C34-22S	C34-22R	C35-22S	C35-22R	Tot.terp.
Adgo	Beaufort-Mackenzie		Canada	BMD01	87	128	293	76	123	186	132	90	162	191	93	52	40	33	46	32	31	20	35	21	14	10	24	11	1930
Adlartok	Beaufort-Mackenzie		Canada	BMD02	34	75	0	22	175	55	41	60	67	275	53	81	56	12	25	37	30	0	19	11	7	10	8	4	1157
Kugpik	Beaufort-Mackenzie		Canada	BMD03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	43	34	31	18	78	39	35	17	21	179	28	69	54	18	24	51	37	22	38	26	23	14	21	17	937
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	27	40	0	22	95	58	22	38	76	190	38	48	42	9	22	24	18	11	15	8	12	7	0	0	822
ISS-0	Beaufort-Mackenzie		Canada	CAN06	117	167	57	168	452	211	100	113	265	857	171	201	162	58	70	97	72	25	58	42	22	19	14	7	3525
ISS-3	Beaufort-Mackenzie		Canada	CAN07	2	4	3	13	3	4	0	4	4	8	2	1	2	0	1	1	0	1	1	0	0	0	0	0	54
ISS-4	Beaufort-Mackenzie		Canada	CAN08	125	185	81	309	498	158	109	123	290	972	215	236	190	73	89	117	88	33	75	54	31	25	23	12	4111
Kut-aj	Kutei		Indonesia	KTM01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-IJ	Kutei		Indonesia	KTM02	0	0	0	0	23	0	0	0	31	37	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	91
Kut-v7	Kutei		Indonesia	KTM03	8	11	0	0	25	0	0	0	16	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	80
Asasa	Niger Delta	NE	Nigeria	NDE01	108	163	121	154	710	209	51	112	1296	976	190	212	170	39	72	117	85	59	74	49	42	26	24	0	5059
Edop	Niger Delta	NE	Nigeria	NDE02	70	94	0	117	421	130	15	69	914	576	125	139	99	0	31	67	50	15	37	27	27	15	9	4	3051
Eku	Niger Delta	NE	Nigeria	NDE03	89	131	0	164	527	195	31	90	1134	603	143	140	109	0	24	80	58	34	54	37	39	21	13	11	3727
Etim	Niger Delta	NE	Nigeria	NDE04	54	75	0	63	303	94	18	51	494	415	89	101	75	0	22	54	41	16	33	28	18	12	8	8	2072
Inanga	Niger Delta	NE	Nigeria	NDE05	40	58	0	118	271	54	10	48	625	360	80	67	55	0	20	35	28	13	21	14	13	7	4	5	1946
Ubit	Niger Delta	NE	Nigeria	NDE06	74	121	0	106	492	135	51	101	723	622	135	152	113	21	39	87	64	29	53	38	32	22	14	11	3235
Unam	Niger Delta	NE	Nigeria	NDE07	74	109	0	167	422	140	51	85	788	517	128	124	90	22	35	70	52	26	47	33	35	25	15	17	3072
Yoho	Niger Delta	NE	Nigeria	NDE08	141	223	292	524	970	304	144	128	2520	1227	253	192	157	17	52	108	83	38	56	33	25	15	0	0	7502
Dibi-6	Niger Delta	NW	Nigeria	NDW09	27	25	0	7	105	31	3	19	87	185	28	44	32	0	11	28	20	6	16	14	8	5	2	2	705
Dibi-11	Niger Delta	NW	Nigeria	NDW10	53	54	0	23	216	65	25	37	154	347	56	91	71	0	26	54	41	0	37	24	17	13	9	4	1417
Gbokoda	Niger Delta	NW	Nigeria	NDW11	210	191	103	99	974	296	103	167	654	1454	240	359	291	100	108	232	172	60	141	97	68	39	38	32	6228
Malu-27h	Niger Delta	NW	Nigeria	NDW12	103	126	118	59	503	144	69	93	728	592	122	113	89	9	28	64	50	16	39	30	20	14	10	7	3146
Malu-28	Niger Delta	NW	Nigeria	NDW13	57	65	0	124	252	81	37	51	464	302	74	61	49	17	21	36	27	14	20	15	16	8	6	3	1800
Mer-12D	Niger Delta	NW	Nigeria	NDW14	77	82	0	124	329	115	47	98	291	418	83	93	72	29	20	58	43	21	34	27	24	16	14	12	2127
Meren-14	Niger Delta	NW	Nigeria	NDW15	115	126	0	231	418	181	74	105	393	556	125	133	110	57	51	85	64	34	59	35	34	23	22	16	3047
KC-W17	Niger Delta	Central	Nigeria	NDC16	98	124	0	116	490	140	20	103	659	646	131	118	94	38	57	45	10	49	22	12	19	9	7	9	3016
KC-19t	Niger Delta	Central	Nigeria	NDC17	92	131	59	46	483	130	58	75	619	633	118	103	82	13	38	52	41	19	29	21	14	8	7	3	2874
Oropouche	Ref. oil	Trinidad	Trinidad &	TRO01	34	41	46	13	115	38	27	24	32	188	37	51	40	0	43	32	23	26	24	16	13	9	9	10	891
Alba	Ref. oil	North Sea	UK	NSA02	87	64	70	27	146	76	54	29	26	239	47	115	89	20	31	105	71	31	80	60	54	37	64	40	1662
Andrew	Ref. oil	North Sea	UK	NSA03	27	11	0	10	24	21	19	2	4	64	10	28	22	10	10	26	20	17	27	18	12	9	11	8	410
NSA-74	Ref. oil	North Sea	n/a	NSA04	34	15	0	10	31	24	19	0	0	78	13	37	28	16	12	32	22	13	24	14	16	8	14	10	470
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	38	22	0	36	69	32	28	10	0	158	21	54	42	8	20	43	29	16	38	25	19	11	16	10	745

IIIb: Sterane and Diasterane Data

					Steranes (ppm)												
Sample Name	Basin	Region	Country	Sample ID	C27aa20S	C27bb20R	C27bb20S	C27aa20R	C28aa20S	C28bb20R	C28bb20S	C28aa20R	C29aa20S	C29bb20R	C29bb20S	C29aa20R	Tot.Ster.
Adgo	Beaufort-Mackenzie		Canada	BMD01	21	105	34	100	14	45	91	49	128	105	89	137	918
Adlartok	Beaufort-Mackenzie		Canada	BMD02	10	50	16	48	0	16	17	13	44	41	21	52	269
Kugpik	Beaufort-Mackenzie		Canada	BMD03	0	31	16	0	0	21	23	0	0	22	19	0	132
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	52	105	120	43	60	69	88	51	69	65	66	57	845
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	3	15	9	7	21	9	15	23	29	31	17	45	224
ISS-0	Beaufort-Mackenzie		Canada	CAN06	21	83	39	82	41	32	44	47	88	66	48	140	731
ISS-3	Beaufort-Mackenzie		Canada	CAN07	1	2	2	2	0	2	1	3	2	4	0	9	28
ISS-4	Beaufort-Mackenzie		Canada	CAN08	27	102	57	107	55	47	65	76	123	119	75	164	1017
Kut-aj	Kutei		Indonesia	KTM01	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-IJ	Kutei		Indonesia	KTM02	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-v7	Kutei		Indonesia	KTM03	0	0	0	0	0	0	0	0	0	0	0	0	0
Asasa	Niger Delta	NE	Nigeria	NDE01	48	63	39	64	59	47	49	55	79	63	45	92	703
Edop	Niger Delta	NE	Nigeria	NDE02	29	28	26	29	35	22	26	28	39	39	22	46	369
Eku	Niger Delta	NE	Nigeria	NDE03	34	33	21	34	36	38	30	33	55	48	24	55	441
Etim	Niger Delta	NE	Nigeria	NDE04	28	26	20	30	27	21	23	29	40	34	21	38	337
Inanga	Niger Delta	NE	Nigeria	NDE05	11	12	7	11	11	6	8	10	22	16	10	21	145
Ubit	Niger Delta	NE	Nigeria	NDE06	45	39	28	59	47	46	32	56	64	52	28	76	572
Unam	Niger Delta	NE	Nigeria	NDE07	41	37	23	53	45	44	29	50	58	53	27	70	530
Yoho	Niger Delta	NE	Nigeria	NDE08	6	28	14	20	20	11	18	18	26	33	25	52	271
Dibi-6	Niger Delta	NW	Nigeria	NDW09	10	9	8	13	9	7	8	11	15	12	7	15	124
Dibi-11	Niger Delta	NW	Nigeria	NDW10	19	18	14	22	19	15	13	21	30	22	12	26	231
Gbokoda	Niger Delta	NW	Nigeria	NDW11	65	72	50	89	71	71	63	87	141	90	89	99	987
Malu-27h	Niger Delta	NW	Nigeria	NDW12	18	25	19	23	23	21	20	26	42	37	22	40	316
Malu-28	Niger Delta	NW	Nigeria	NDW13	13	14	9	15	15	16	11	15	23	19	8	25	183
Mer-12D	Niger Delta	NW	Nigeria	NDW14	21	22	18	28	19	20	17	23	39	25	17	37	286
Meren-14	Niger Delta	NW	Nigeria	NDW15	37	33	27	39	30	37	27	33	58	42	22	53	438
KC-W17	Niger Delta	Central	Nigeria	NDC16	30	30	18	38	26	32	22	36	43	36	18	54	383
KC-19t	Niger Delta	Central	Nigeria	NDC17	22	25	19	31	26	26	20	36	41	41	20	37	344
Oropouche	Ref. oil	Trinidad	Trinidad & Tobego	TRO01	45	52	52	58	51	59	50	55	53	50	42	56	623
Alba	Ref. oil	North Sea	UK	NSA02	51	116	86	43	59	55	67	42	90	90	73	50	822
Andrew	Ref. oil	North Sea	UK	NSA03	22	60	46	61	20	20	31	16	28	28	24	19	375
NSA-74	Ref. oil	North Sea	n/a	NSA04	20	63	41	61	18	21	32	15	26	30	22	14	363
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	19	63	41	59	18	27	38	19	37	46	33	21	421

					Diasteranes (ppm)																		
Sample Name	Basin	Region	Country	Sample ID	C27-20S	C27-20R	C28-20S-a	C28-20S-b	C28-20R-a	C28-20R-b	C29-20S	C29-20R	Tot.Diast.	C27-20S+R	C28-20S+R	C29-20S+R	%C27-dia	%C28-dia	%C29-dia
Adgo	Beaufort-Mackenzie		Canada	BMD01	25	16	15	22	10	10	95	89	282	41	56	184	15	20	65
Adlartok	Beaufort-Mackenzie		Canada	BMD02	15	10	5	10	4	11	49	42	146	25	29	91	17	20	63
Kugpik	Beaufort-Mackenzie		Canada	BMD03	49	33	32	35	23	18	49	38	277	82	109	87	30	39	31
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	84	56	64	69	42	36	88	74	513	140	211	163	27	41	32
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	15	7	9	9	7	8	19	18	92	23	34	37	24	36	40
ISS-0	Beaufort-Mackenzie		Canada	CAN06	37	28	33	34	16	26	93	64	331	65	109	157	20	33	47
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISS-4	Beaufort-Mackenzie		Canada	CAN08	58	37	42	47	28	32	90	61	395	95	150	151	24	38	38
Kut-aj	Kutei		Indonesia	KTM01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-IJ	Kutei		Indonesia	KTM02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kut-v7	Kutei		Indonesia	KTM03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Asasa	Niger Delta	NE	Nigeria	NDE01	31	23	21	30	10	17	66	43	241	55	77	110	23	32	45
Edop	Niger Delta	NE	Nigeria	NDE02	14	9	9	13	0	19	27	25	116	22	41	52	19	35	45
Eku	Niger Delta	NE	Nigeria	NDE03	20	12	10	16	5	9	32	32	136	32	40	64	23	29	47
Etim	Niger Delta	NE	Nigeria	NDE04	15	8	7	13	0	11	25	23	102	24	31	47	23	30	46
Inanga	Niger Delta	NE	Nigeria	NDE05	7	4	4	6	0	6	13	12	52	11	16	26	20	31	49
Ubit	Niger Delta	NE	Nigeria	NDE06	22	15	12	17	6	14	35	34	155	36	49	69	24	32	45
Unam	Niger Delta	NE	Nigeria	NDE07	22	11	11	16	5	13	36	32	146	32	46	68	22	31	47
Yoho	Niger Delta	NE	Nigeria	NDE08	15	7	8	10	4	6	34	21	105	22	28	55	21	27	52
Dibi-6	Niger Delta	NW	Nigeria	NDW09	7	4	4	4	0	6	10	7	42	11	14	17	26	33	41
Dibi-11	Niger Delta	NW	Nigeria	NDW10	8	5	4	7	0	7	17	12	60	13	18	29	22	30	48
Gbokoda	Niger Delta	NW	Nigeria	NDW11	33	23	18	26	8	15	69	38	230	55	67	106	24	29	47
Malu-27h	Niger Delta	NW	Nigeria	NDW12	7	5	6	4	4	2	10	10	48	13	16	20	26	33	41
Malu-28	Niger Delta	NW	Nigeria	NDW13	8	5	4	7	2	4	15	15	60	13	17	29	22	29	49
Mer-12D	Niger Delta	NW	Nigeria	NDW14	11	7	6	10	0	10	19	17	80	18	26	36	22	33	45
Meren-14	Niger Delta	NW	Nigeria	NDW15	18	12	9	18	0	15	31	33	136	30	42	65	22	31	47
KC-W17	Niger Delta	Central	Nigeria	NDC16	15	11	9	12	0	11	26	27	111	26	32	53	24	29	47
KC-19t	Niger Delta	Central	Nigeria	NDC17	9	6	7	5	3	3	10	12	55	15	18	21	27	33	39
Oropouche	Ref. oil	Trinidad	Trinidad & Tobego	TRO01	19	13	12	12	8	8	18	17	107	32	40	35	30	38	33
Alba	Ref. oil	North Sea	UK	NSA02	63	40	31	28	15	22	57	45	301	104	97	102	34	32	34
Andrew	Ref. oil	North Sea	UK	NSA03	74	57	40	44	24	25	86	57	407	130	133	143	32	33	35
NSA-74	Ref. oil	North Sea	n/a	NSA04	77	48	41	36	21	23	73	35	354	125	121	108	35	34	30
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	62	39	33	42	19	21	83	48	347	101	114	131	29	33	38

IIIb: Aromatic Hydrocarbon Data

Aromatic Hydrocarbons (ppm)

					Naphthalenes																	
Sample Name	Basin	Region	Country	Sample ID	Naph.	2-MN	1-MN	2-EN	1-EN	2,6+2,7-DMN	1,3+1,7-DMN	1,6-DMN	1,4+2,3-DMN	1,5-DMN	1,2-DMN	1,3,7-TMN	1,3,6-TMN	1,4,6+1,3,5-TMN	2,3,6-TMN	1,2,7+1,6,7+1,2,6-TMN	1,2,4-TMN	1,2,5-TMN	1,2,3-TMN
Adgo	Beaufort-Mackenzie		Canada	BMD01	0.2	0.2	0.1	0	0	0.2	0.3	0.3	0.3	0.1	0.2	0.7	0.4	0.6	2.7	1.3	0.8	0.6	1.7
Adlartok	Beaufort-Mackenzie		Canada	BMD02	5.4	48.2	21.1	1.1	0.7	111.6	120.3	60.9	51.9	9.3	17.5	121.3	121.7	92.2	140.9	216.6	10.9	56.5	15.5
Kugpik	Beaufort-Mackenzie		Canada	BMD03	1.8	15.9	6.8	1.1	0.4	55.3	47.8	27	19.5	3.8	5.2	63.4	71.8	39.7	79.1	76.3	3.3	10.2	3.8
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	0.9	8.3	5.8	0.6	0.3	20.3	28.9	18.1	11.1	3.6	5.1	26.1	41.7	31.1	31.3	62.3	2.9	12.1	4.6
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	0.1	0.2	0.1	0.1	0	0.4	0.4	0.3	0.2	0.1	0.1	0.4	0.5	0.4	0.7	1.3	0.1	0.2	0.1
ISS-0	Beaufort-Mackenzie		Canada	CAN06	0.1	0.3	0.1	0	0	2.7	3.1	1.8	1.6	0.3	0.5	6.3	8.7	4.8	5.5	17.1	0.6	5.1	1.2
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	1.6	1.9	0.4	0.3	5.4	13	3.9	5.6	1.3	1.3	15.6	12.5	10.5	8	23.6	0.8	5.6	1.2
ISS-4	Beaufort-Mackenzie		Canada	CAN08	0.1	0.6	0.4	0.1	0	1.9	2.3	1.4	1.3	0.2	0.4	4.8	6.9	3.6	4.4	14.3	0.5	3.7	1.2
Kut-aj	Kutei		Indonesia	KTM01	0.2	16.6	9.3	0.6	0	68.8	69.7	120	34.2	5.2	14.3	59.8	78.1	61.8	66	225.5	5.1	51.1	7
Kut-IJ	Kutei		Indonesia	KTM02	0.1	1.7	1	0.3	0	17.6	23.8	23.9	9.8	7	6.7	136.5	221.7	198.1	149.6	270	17.9	72	13.6
Kut-v7	Kutei		Indonesia	KTM03	9.7	72.5	33.7	2.9	1.1	146.9	138.9	186.6	57.9	9.8	19.7	137.7	166.3	117.7	165.9	373.7	9.3	70	13.7
Asasa	Niger Delta	NE	Nigeria	NDE01	4.6	30.3	15.2	1.3	0.6	62.8	64.8	45.4	30.7	5.6	11	51.5	68.8	47.6	71.7	115.8	5.4	26.2	7.7
Edop	Niger Delta	NE	Nigeria	NDE02	11.8	138.3	72.6	4.5	3.7	388.8	373.3	282.7	150.5	46	64.5	229.8	344.1	224.3	257	439.4	26.3	120.5	24
Eku	Niger Delta	NE	Nigeria	NDE03	5	105.6	64.9	4.9	3.1	304.5	291.2	247.9	117	36.6	42.9	194.8	299.2	11.7	200	387.1	24.9	117.9	23.3
Etim	Niger Delta	NE	Nigeria	NDE04	119.3	782.2	426	37.6	20.3	642.2	671	587.6	211.9	97.9	90.6	223.6	348.7	241.2	219.3	367.5	27.9	112.2	22.3
Inanga	Niger Delta	NE	Nigeria	NDE05	5.4	73.5	49.4	5.2	4	158.8	206.7	166.8	63.4	33.7	35.7	98.7	164.9	110.2	85.4	211.5	13.6	80.4	12.5
Ubit	Niger Delta	NE	Nigeria	NDE06	1.2	49.6	38.8	3.7	3.6	212.1	248.9	219.4	89.1	40.9	45.4	148.3	245	170.6	156.7	294.1	21.3	102.7	19.1
Unam	Niger Delta	NE	Nigeria	NDE07	15.1	158.6	79	5.5	5	284.3	296.2	273.2	100.6	46.4	55.2	134.5	228	154.5	139.2	281.6	20.2	100.7	16.6
Yoho	Niger Delta	NE	Nigeria	NDE08	71.4	151.6	96.4	12.4	5.1	118.9	123.7	94.1	46.1	15.3	19.5	46.5	67	48.1	45.9	89.7	7.3	33.7	6.3
Dibi-6	Niger Delta	NW	Nigeria	NDW09	6.6	89.4	46	3.3	2.3	242.1	230.2	184.9	73.4	30.2	30.9	129.8	195.6	130.7	126.2	211.5	14	65.4	14.8
Dibi-11	Niger Delta	NW	Nigeria	NDW10	15.5	126.2	69.4	4.9	3.8	249.3	235.1	196.9	78.7	32.9	38.1	125	194.4	8.9	129.5	219	14.9	80.2	13.1
Gbokoda	Niger Delta	NW	Nigeria	NDW11	39.4	160.4	82.1	9.4	3.7	280.4	294.4	212	114.3	28.7	41.6	191.1	238.7	180	211.8	332.7	16.6	97.5	19.4
Malu-27h	Niger Delta	NW	Nigeria	NDW12	8.1	37.3	17.7	1.9	0.6	73.2	67	43.7	32.6	4	10.1	68.7	80.8	41.4	82.4	154.2	5.3	39.4	8.8
Malu-28	Niger Delta	NW	Nigeria	NDW13	139.6	661.5	283.7	22.3	12.4	982.2	770.3	550.5	302	80.5	115	443.3	605.9	348.1	453.1	744.2	38.7	217.2	31.1
Mer-12D	Niger Delta	NW	Nigeria	NDW14	25.4	149.1	100.1	7.2	6.9	367.2	338.8	220.7	118.6	57.2	48.3	170.2	256.1	183.4	140.3	285.1	19.8	104.7	16.8
Meren-14	Niger Delta	NW	Nigeria	NDW15	27.1	197	80.4	6.1	4.5	515.3	404.4	260.3	174	52.7	61.9	306	413	246.1	335.4	491.4	25.4	116.8	28.4
KC-W17	Niger Delta	Central	Nigeria	NDC16	47.7	108.6	73.3	12.3	9.4	790.6	755.1	544.6	324.3	93	115.3	860.7	1086.9	642.2	917.4	1378.8	64.5	498.3	62.8
KC-19t	Niger Delta	Central	Nigeria	NDC17	0.7	4.6	1.9	0	0.2	21.9	18.7	11	11.1	0.9	3	40.9	44.6	16.3	63.1	99.4	2.6	26.1	5.5
Oropouche	Ref. oil	Trinidad	Trin./ Tobego	TRO01	1.5	22.7	8.3	0.6	0.2	93.7	78.9	45.3	42	5.2	11.7	106.3	109.1	58.1	116.2	177.1	6.4	29.2	11.7
Alba	Ref. oil	North Sea	UK	NSA02	0.2	0.3	0.2	0	0	4.1	6	3.1	4	0.8	2	26.3	28.5	28.8	29.2	55.2	7.5	16.7	9.6
Andrew	Ref. oil	North Sea	UK	NSA03	0.3	1.8	0.9	0.1	0	9.1	8.7	5.9	4.8	0.8	1.5	9.8	13	7.4	10.7	18.9	0.8	3.2	1.2
NSA-74	Ref. oil	North Sea	n/a	NSA04	38.7	183.8	115.9	10.4	2.5	276	319.3	215.3	114.3	44	40.4	160.9	201.8	134.7	132.9	222.7	13.5	47.5	12.4
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	5.3	21.4	12.2	1	0.4	30.4	34.4	24.2	17	3.1	5.4	26.4	33.6	41.5	32.5	60.6	3	16	4.9

IIIb: Aromatic Hydrocarbon Data (Cont'd)

Aromatic Hydrocarbons (ppm)																																					
Phenanthrenes															Dibenzothiophenes										Biphenyls						Fluorenes					
Phen.	3-MP	2-MP	9-MP	1-MP	3,6-DMP + (2+3+1EP)	2,6-+ 3,5-DMP	2,7-DMP	3,10+1,3+2 ,10+3,9-	1,6+2,5+2, 9-DMP	1,7-DMP	2,3-DMP	1,9+4,9+4, 10-DMP	1,8-DMP	?DMP*	DBT	4-MDBT	3-,+2-MDBT	1-MDBT	?4-EDBT	?4,6-DMDBT	2,4+2,6-DMDBT	1,4-DMDBT	1,3-DMDBT	Biphenyl	2-MB	DPM	3-MB	4-MB	DBF	Fluorene	3-+2-MF	1-MF	4-MF	Tot.AroHC
4.2	7.9	17.5	66.4	7.3	78.5	28.2	68.1	307.4	96.5	44.8	64.8	59.6	5	4.3	1.2	6.9	0.4	0.4	3.6	3.5	0.4	0.3	0.9	0.1	0.2	0.1	0.3	0.1	0.1	3	4.2	7.8	10.2	915
125.8	76.4	77.1	69.9	49.8	35.8	43.9	22.1	101.3	49.2	40.5	18.3	16	6.6	5.5	1.8	9.5	1.8	0.5	2.7	5.6	3	0.4	0.9	58.9	24.6	55.8	262	101.5	38.8	103.8	91.9	132.8	18.7	2877
138.1	110.6	122.8	126.9	93.1	40.8	56.8	32.7	209.3	99.6	65.9	30.8	40.6	16.5	8.4	0.8	2.5	2.5	0.9	0.4	4.9	4.4	1.2	1.1	76.7	9.4	17.5	200	86.4	11.3	41.2	53.3	62.3	10.5	2312
47.4	44.8	35.8	63.8	42.5	24.1	19.4	10.7	107.4	43	29.4	11.9	25.1	11.2	4.8	0.5	2.9	0.3	0.3	0.3	0.9	0.4	0.3	0.1	35.9	22.1	10.4	81.8	31.4	3.5	41.8	46.6	61.7	14.9	1192
49.6	75.3	99.5	63.8	44	36.1	60.8	35.9	119.6	56.2	35.1	28.8	14.4	6.8	5.9	1.6	1.6	26.2	5.9	1.9	53.1	55	12.8	14.2	0.2	0	0.1	0.4	0.3	0.2	14	41.9	55.6	10.5	1033
17.2	4.9	6.5	12.2	7.2	4.3	3.9	2.5	23	7.5	8.1	3.7	4.5	3.8	1.5	0.4	2.9	3.7	0	0.9	0.8	0.4	0	0	3.2	1.4	8.2	38.5	12.5	1.3	24.6	18.9	30.9	4	323
2	0.6	0.7	1	0.7	0.4	0.2	0.1	1.1	0.4	0.4	0.1	0.2	0.2	0.1	0.4	0.3	0.5	0.4	0.1	0.1	0.2	0.1	0	1.9	3.4	1.7	4.3	2.2	0.3	1.8	1.2	1.5	0.4	142
11.6	4.7	6.1	13	7	4.1	3.4	1.8	11.9	6.1	6.6	2	2.7	3.3	1	0.5	2.3	3.3	0	1	0.8	0.4	0.2	0.1	1.9	1.2	5.2	24.6	7.5	0.5	18.6	13	23.6	4.1	242
9.5	4.1	4.4	5.4	3.1	1.3	1.5	0.6	5.3	2.5	1.7	0.7	0.7	0.3	0.3	0.9	3.1	0.6	0.3	1.2	1	0.5	0.2	0.2	54.6	8.3	27.9	170.3	48.1	22	9.9	6.8	18.3	1.9	1311
33.7	7.7	8.4	9.8	5.9	3.5	4.4	2.2	13.4	6.5	5.6	2.3	2.1	0.8	0.6	1.9	3.2	0.4	0.2	0.4	0.8	0.4	0.1	0.1	29.4	2.9	9.6	39.8	18.4	7.6	76.8	90.4	146.6	32.6	1740
58.8	34.6	32.8	47	24.3	20.7	25.4	10.4	72.3	38.1	22.6	13.3	10.4	4.9	3.4	2.1	10.5	0.8	0.6	3.6	4.2	1	0.6	0.5	58.4	7.4	29	288.9	90.9	26.4	33.3	41.3	99.4	10.3	2862
46.6	39.8	38.5	45.2	30.5	19.3	21.6	11.4	91.2	40.1	37.8	13.5	13	5.4	4.6	0.7	4.4	0.4	0.3	0.9	1.5	1	0.1	0.2	14.5	2.8	4.9	43	15.8	6.9	31.1	37.2	59.5	9.7	1360
69.9	42.3	49.2	52.5	46.7	22.2	20.4	12.3	91.6	45.5	41.3	14.4	20.9	9	4.9	9.2	6.4	9.7	8.9	2.4	6.1	12.8	7.1	3.4	29.3	5.3	5	63.9	25.4	16.9	35.3	35.5	59.2	12.8	4100
63.6	45.3	53.5	54.6	42.9	22.3	19.8	13.1	91.8	46.5	46.8	14.6	19.4	9.4	4.2	10.5	7.2	8.7	8.1	2.7	6	13.2	6.5	3.2	46.6	3.4	3.2	37.1	14.8	14.6	31	33.6	48.6	11.8	3341
67.2	38.5	45.1	47.1	38.1	19.3	17.5	11.4	81.1	40.7	36.3	12.9	18.7	9.2	4.5	11.7	5	9.2	7.9	2	4.9	12.1	5.5	2.4	28.3	4.4	4	58	24.5	16.6	30.4	29.5	48.8	10.9	6053
19.2	11	12.7	15	13.1	7.3	7.3	4.9	32.4	18.1	17.3	6	8.7	4	2.1	4.6	3.2	3	3.1	2.2	3.7	4.5	2.1	1.1	2.4	1.5	1.6	25.3	8.5	6.5	7.3	8.5	15.3	3.4	1867
34.3	25.7	29.3	33	27.8	14.8	12.8	8.1	62.9	33.7	31.2	10.8	14.8	7.4	3.7	8.4	5.7	6.3	5.6	2.3	5	9.2	4.6	2.2	6.1	1.9	2.1	25	9.5	7.3	15.7	18.8	34.8	7.9	2639
27	17.4	21.6	25.6	26.1	11.4	9.2	5.7	46.3	23.8	27.6	8.3	10.2	4.7	2.9	7.4	5.9	5.2	4.5	2.2	3.7	6.4	3.3	1.6	5.9	2.6	2.6	22.2	7.6	7	17	16.8	30.2	7	2821
25	19.8	20.3	24.8	17.7	10.5	12.7	7	45.3	22.3	24.1	8.4	8.7	4.2	3	2.2	1.7	2.2	2.2	0.8	1.7	2.4	1.2	0.8	10.6	1.8	2.2	26	9.1	7.1	9.1	12.3	30	3.2	1479
36.7	22.1	32.1	29.6	34.1	10.8	9	10.6	51.7	29.6	25.2	7.1	15.8	5.4	1.9	1.3	2.8	0	0	0	0	0	0	0	26.2	4.2	3.4	62.6	25.5	8	11.2	15.9	30.9	6.5	2347
30.5	18.8	23.6	28.1	24	9.7	9	6.4	48.9	24.1	20	7.8	12.6	5.4	3.2	2.2	3.4	0.2	0.3	0.8	1.2	0.2	0	0	25.6	4.9	3.9	68.2	27.3	10.1	9.6	11.4	23.9	4.8	2306
106.7	83	82.6	107.3	67.3	31.8	37	21.1	165	75.5	65.6	24	28.1	13.6	8	1.7	7.2	0.9	0.5	1.4	3.1	2.1	0.7	1	18.4	10.5	10.2	35.2	16.2	13.2	28.6	51.7	108.8	14.8	3797
38	38.4	36.2	42.6	24.9	19.5	24.1	12.1	94.7	43.1	41.2	14.2	15.1	7.8	4.3	1.5	4.8	2.3	1.2	1.3	3.4	3.8	1.3	1.1	27.3	5.5	8.3	101.3	36.4	9.2	26.7	26.7	65.1	8.4	1569
200.4	125.8	141.8	149.9	108.8	47.7	61.1	39.9	232.8	116.5	97.5	36.2	45.6	20.5	10.2	4	9	0.9	0	2.1	3.8	1	0	0	141.3	10.4	12	267.1	108.8	48.1	67.6	71.9	126.6	20.6	9132
48.6	41.2	52.1	57.4	40.5	21.5	23.6	16.1	103.4	50.4	42.9	18.1	22.9	10.6	5.1	8.6	5.4	10.2	6.8	2.7	8.5	14.1	7	3.4	6.8	4.2	3.8	22.4	11.2	5.1	18	21	38	9.4	3377
168.7	127	149.5	160.2	109.8	53.7	62.3	42.2	256.6	121.5	100.9	40.9	51.3	23.6	11.7	4.9	8.3	4.7	1.1	2.3	9.1	8.1	2.3	2	38.4	8.7	6.4	95.3	48.4	17	56.9	64.3	112.8	23.8	5741
434	250.9	269.7	252.7	185.2	87.9	109.7	65.7	366.1	173.8	150.8	55.8	66.7	31.7	14.3	11.9	18.8	1.8	1.2	5.1	5.8	0.9	0	0	132.6	14.7	21.7	744.4	262	112.2	119.5	147.7	282.5	38.8	12822
91.4	84.7	88.2	84	59.3	35.3	53.1	28.2	156	73.8	70.3	26.5	26.1	12.8	6.9	2.9	6	6.5	4.5	1.5	7.3	8.8	2.4	2.2	41.9	5.7	25.4	201.7	85	11.2	57.3	64.5	147.7	16.3	1968
257.1	271.5	203.1	216.9	152.8	87.2	94.6	58.2	404.8	159.7	137.3	51.6	53.7	30.1	17.4	10.8	5	26.4	18.5	3.3	24.8	40.2	14.5	12.3	146.9	16.5	15.9	329.6	142.9	11.1	125.5	129.5	217	34.6	4446
112.4	96.1	95.9	204.2	84.6	63.4	57.1	37.5	306.8	117.3	68.5	25.7	64.3	23.2	12.2	24.8	8.5	68.9	43.6	14.6	67.7	81.7	60.8	28	1.5	1.5	2.4	12.1	6.1	2.4	29.7	57.9	101.7	19.6	2225
49.3	54.7	58.7	87.2	66.9	27.1	40.7	26.2	189.8	87.9	62.6	25.5	42.1	20.6	10	1.1	1.6	3.4	2.2	0.4	3.2	5.3	2.1	2.1	23.7	8.6	23.2	68.8	32	1.8	65.1	84.1	119.7	23.9	1421
330.7	161.6	156.9	263	174.3	57.5	52.5	32.5	275.6	125.5	85.8	35.3	56.9	30.7	11.8	24.4	2.4	58.6	26.2	6.5	39.5	51.5	25.6	14.4	230	43.2	23	238.6	91.3	28.1	129	68.2	130.2	29.5	5398
99.3	58.2	64.5	89.9	70.2	19.5	19.4	7.9	94.9	44	35.9	12.5	20.9	10	5.8	2	1.6	3.9	3.3	0.4	4.5	7.8	3.3	2.5	78.7	13.4	13.9	133.2	47.4	7.4	82.8	46.8	66	14.1	1559

IIIb: Aromatic Steroid Hydrocarbon Data

					Triaromatic Steroid HCs (ppm)											Monoaromatic Steroid HCs (Peak area)									
Sample Name	Basin	Region	Country	Sample ID	20TAS	21TAS	22TAS(a+b)	C26-20S	C26R+C27S	C28-20S	C27-20R	C29(a+b)-20S	C28-20R	C29-20R	Tot.TAS	21MAS	22MAS	C27βS	C27dia-S	C27βR+	C28βS+	C28βR+	C29α-20S	C28αR+C29βR	C29αR
Adgo	Beaufort-Mackenzie		Canada	BMD01	2.9	1.4	10.5	0.6	2.7	5.9	2	0	5.1	0	31.1	335556	359639	345008	0	0	1353572	3117114	953131	2249248	889541
Adlartok	Beaufort-Mackenzie		Canada	BMD02	1.1	0.9	4.8	0.2	2.6	4.1	1.5	0	3.8	0.2	19.2	110205	75153	109026	0	102837	277287	718938	120069	386960	254282
Kugpik	Beaufort-Mackenzie		Canada	BMD03	6.2	3.8	0.7	0.6	1.1	0.8	0.2	0	0.6	0.1	14.1	150501	118523	26882	60115	115599	176214	181939	39001	77413	20100
Mayogiak	Beaufort-Mackenzie		Canada	BMD04	5.1	6.3	1.8	1.7	7.8	4	6.9	2.2	4.9	1.8	42.5	371283	291074	328711	0	0	275150	2187554	155760	558533	97325
Tarsiut	Beaufort-Mackenzie		Canada	BMD05	0.1	0.2	0.2	0.1	0.4	0.5	0.4	0	0.6	0.1	2.6	164229	119968	145994	0	0	95658	1206161	194928	437505	319312
ISS-0	Beaufort-Mackenzie		Canada	CAN06	1.2	1.2	0	0.5	1.4	1.7	1	0	1.9	0.2	9.1	163135	209374	19222	107171	32684	420568	946576	244927	502938	193553
ISS-3	Beaufort-Mackenzie		Canada	CAN07	0	0	0	0	0.1	0	0	0	0	0	0.1	18644	7030	10338	0	5077	25920	54114	14727	25638	12383
ISS-4	Beaufort-Mackenzie		Canada	CAN08	0.8	0.9	1.1	0.6	2.5	2.8	1.9	0.7	3.5	0.8	15.6	196020	312526	397451	0	85472	1070285	2079743	561533	1030011	462589
Kut-aj	Kutei		Indonesia	KTM01	0	0	0	0	0.1	0.1	0	0	0.1	0	0.3	10245	0	0	0	0	0	0	0	0	0
Kut-IJ	Kutei		Indonesia	KTM02	0.1	0.1	0	0.1	0.6	0.6	0.1	0	0.5	0	2.1	8361	0	0	0	0	18983	54354	16828	35538	8496
Kut-v7	Kutei		Indonesia	KTM03	1.5	0.8	0.5	0	0.3	0.2	0	0	0.2	0	3.5	88644	39476	0	0	0	26879	74186	11650	28435	0
Asasa	Niger Delta	NE	Nigeria	NDE01	4.2	2.8	1.2	4	12.5	9.2	7.8	2.3	10.3	0.8	55.1	479123	192761	274928	197368	411666	1236359	2235588	688599	1069392	413664
Edop	Niger Delta	NE	Nigeria	NDE02	7.6	6.4	3.2	11.2	33.9	27.3	17.6	6.6	24	1.6	139.4	241967	65927	207001	126351	260334	715700	1408377	422375	644646	259995
Eku	Niger Delta	NE	Nigeria	NDE03	8.1	5.6	3.6	15.5	46.3	39.2	25.6	10	33.2	2	189.1	223048	144329	374459	251798	482398	1308489	2987197	775084	1228567	441067
Etim	Niger Delta	NE	Nigeria	NDE04	7.2	5.8	2.8	12.7	37	26.4	19.3	7.7	23.8	1.8	144.5	219725	57844	245256	131269	278024	850737	1705401	427774	658491	244223
Inanga	Niger Delta	NE	Nigeria	NDE05	2.6	2.2	0.3	4.8	13.8	15.3	7.6	3.3	12.5	0.6	63	81129	48970	24772	64040	88903	250443	562127	151237	290754	101631
Ubit	Niger Delta	NE	Nigeria	NDE06	7.6	6.6	3.6	20.2	60.2	41.2	30.4	11.9	39.8	3.6	225.1	298966	90113	266972	300379	515983	1574780	2204091	875257	1328696	504587
Unam	Niger Delta	NE	Nigeria	NDE07	5.9	4.3	2.6	17.5	55.9	40.2	27.6	11	35	2.7	202.7	274976	79325	244337	263885	493791	1461340	3251508	819395	1283666	479464
Yoho	Niger Delta	NE	Nigeria	NDE08	1.7	0.8	0.3	0.9	4.1	4.8	2.8	1.5	4.4	0	21.3	111518	40439	192866	0	0	632794	1028351	354965	530115	235394
Dibi-6	Niger Delta	NW	Nigeria	NDW09	3	2.1	1.4	3.8	9.5	7.4	5.4	2.6	6.8	0.6	42.6	67980	31650	86588	51650	95754	287160	562277	135082	220095	103337
Dibi-11	Niger Delta	NW	Nigeria	NDW10	3.3	2.7	1.7	6.1	17.9	12.5	9	4.3	11.8	1.7	71	116154	46194	95733	119166	176578	481744	851389	244870	391934	179917
Gbokoda	Niger Delta	NW	Nigeria	NDW11	6.6	5.2	1.4	6.5	18.4	14.4	10.9	4.7	14.9	1.2	84.2	204580	93842	235716	184727	319430	873485	1595950	528566	758454	312548
Malu-27h	Niger Delta	NW	Nigeria	NDW12	2.2	1.2	1.2	1.4	4.2	3.7	2.6	1	4	0.2	21.7	180517	75954	54769	50545	110909	286978	732112	225832	354030	173574
Malu-28	Niger Delta	NW	Nigeria	NDW13	7	6	1	5.8	17.8	14.5	8.6	3.3	12.2	0	76.2	444324	185692	430828	296499	576719	1264141	2822950	940842	1399537	557294
Mer-12D	Niger Delta	NW	Nigeria	NDW14	6.9	5.8	2.4	11.9	33.4	24.9	16.3	7	22.4	1.2	132.2	249942	132697	300814	192700	398010	1107487	2429526	690481	995508	422505
Meren-14	Niger Delta	NW	Nigeria	NDW15	13	12	5.1	15.6	46.9	33	24.7	10	30.8	2.1	193.2	177258	48317	117776	81314	145367	454066	893416	305764	435466	198418
KC-W17	Niger Delta	Central	Nigeria	NDC16	9	6	1.6	6.6	18.3	18.4	10.5	4.8	14.9	0	90.1	123692	35745	79770	53305	103202	346776	766633	219080	332238	126606
KC-19t	Niger Delta	Central	Nigeria	NDC17	2	0.9	0	0.8	2.5	2.3	1.3	0.7	2.3	0.1	12.9	120011	21720	30988	29521	71381	250737	510612	165480	255977	129507
Oropouche	Ref. oil	Trinidad	Trinidad & Tob	TRO01	7.6	5.5	1.7	1.7	6.5	3.7	5	1.3	4.7	0.4	38.1	199226	80895	113408	57868	128847	370774	685282	184932	308130	103461
Alba	Ref. oil	North Sea	UK	NSA02	15.4	15.5	6.5	7.8	29.8	17.5	20.5	7.7	19.7	4.8	145.2	1383130	594384	576645	1471873	2267825	4424443	7108932	618900	2943709	619209
Andrew	Ref. oil	North Sea	UK	NSA03	4.9	4.4	0	1	1.6	1	1	0	1	0.4	15.3	184699	121891	85270	0	0	173629	222090	13959	102787	10121
NSA-74	Ref. oil	North Sea	n/a	NSA04	9.8	10.3	1.9	1.7	7.8	5.3	4.9	2	4.8	1	49.5	138458	66237	79924	0	0	134241	194036	10189	74190	10828
Veslfrikk	Ref. oil	North Sea	Norway	NSV05	3.7	3.3	0.9	0.6	2.7	2.2	1.9	0.8	2.6	0.6	19.3	157499	110341	83732	0	0	175486	282519	26325	128716	20342

IIIb: Biomarker Parameter Data I

					Normal and Isoprenoid Alkane ratios									Sterane and Diastertane ratios															
Sample Name	Basin	Region	Country	Sample ID	Pr/Ph	Pr/C17	Ph/C18	C12/(C12-27) (%)	C17/C27	C17-C19 /C27-C29	CPI-1	CPI-2	CPI-3	DiaSt	St29S/R	St29I/R	abbC29-St	27St217	28St217	29St217	%C27st	%C28st	%C29st	20S-C27	20S-C28	20S-C29	St29/Tt30	C27dia	C28dia	C29dia
Adgo	Beaufort-Mackenzie		Canada	**BMD01**	0.36	0.83	1.04	19.72	26.47	78.37	1.57	2.37	2.01	8.23	0.93	0.73	0.42	0.54	0.21	0.92	34.96	17.09	47.95	0.17	0.22	0.48	0.91	14.64	20.00	65.36
Adlartok	Beaufort-Mackenzie		Canada	**BMD02**	3.30	2.42	1.25	10.03	20.89	22.77	1.69	1.10	1.79	13.86	0.85	0.65	0.39	0.74	0.13	0.85	42.52	11.46	46.02	0.18	0.00	0.46	0.22	17.42	19.97	62.61
Kugpik	Beaufort-Mackenzie		Canada	**BMD03**	1.66	0.63	0.43	8.19	5.19	6.67	0.83	1.04	0.94	66.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	29.56	39.21	31.23
Mayogiak	Beaufort-Mackenzie		Canada	**BMD04**	1.63	1.06	0.86	7.26	3.61	3.67	0.96	0.98	1.00	35.19	1.22	1.04	0.51	0.40	0.51	0.60	28.66	33.85	37.49	0.54	0.54	0.55	2.29	27.22	41.14	31.64
Tarsiut	Beaufort-Mackenzie		Canada	**BMD05**	1.09	0.63	0.70	12.37	143.21	161.20	0.90	1.16	0.98	15.69	0.64	0.63	0.39	0.10	0.43	1.53	9.28	30.26	60.46	0.30	0.48	0.39	0.28	24.16	36.14	39.71
ISS-0	Beaufort-Mackenzie		Canada	**CAN06**	4.13	1.44	0.40	2.70	4.42	5.38	1.25	1.30	1.36	15.14	0.63	0.50	0.33	0.44	0.21	1.08	30.47	17.62	51.91	0.20	0.46	0.39	0.14	19.43	32.40	48.17
ISS-3	Beaufort-Mackenzie		Canada	**CAN07**	5.08	4.35	10.68	11.67	44.15	54.32	0	0.60	0.00	0.00	0.25	0.38	0.27	0.16	0.27	1.88	13.59	21.10	65.30	0.34	0.00	0.20	0.39	0.00	0.00	0.00
ISS-4	Beaufort-Mackenzie		Canada	**CAN08**	3.97	7.53	13.14	8.43	3.41	2.91	1.18	1.48	1.60	15.04	0.75	0.68	0.40	0.45	0.28	0.89	30.90	21.93	47.18	0.20	0.42	0.43	0.23	23.62	37.16	39.22
Kut-aj	Kutei		Indonesia	**KTM01**	11.22	1.42	0.21	24.48	0.00	0.00	0	3.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Kut-IJ	Kutei		Indonesia	**KTM02**	10.35	0.24	0.19	0.84	148.46	78.40	0.92	0.88	0.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Kut-v7	Kutei		Indonesia	**KTM03**	6.08	1.12	0.24	6.39	21.34	28.50	0.93	1.15	1.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Asasa	Niger Delta	NE	Nigeria	**NDE01**	2.87	1.65	0.70	6.78	2.97	3.00	1.09	1.21	1.14	16.31	0.86	0.63	0.39	0.43	0.35	0.77	30.23	26.12	43.65	0.43	0.52	0.46	0.03	22.59	32.06	45.35
Edop	Niger Delta	NE	Nigeria	**NDE02**	2.78	1.51	0.58	6.15	1.68	1.67	1.17	1.14	1.15	13.10	0.85	0.72	0.42	0.40	0.37	0.81	28.34	26.82	44.84	0.50	0.56	0.46	0.01	19.19	35.33	45.48
Eku	Niger Delta	NE	Nigeria	**NDE03**	3.01	1.52	0.56	5.35	1.31	1.38	1.14	1.13	1.13	14.82	0.99	0.65	0.40	0.38	0.37	0.83	27.57	26.94	45.49	0.50	0.52	0.50	0.01	23.48	29.31	47.21
Etim	Niger Delta	NE	Nigeria	**NDE04**	2.69	1.27	0.54	9.34	1.74	1.66	1.14	1.12	1.12	15.15	1.04	0.70	0.41	0.44	0.43	0.65	30.70	30.07	39.23	0.48	0.48	0.51	0.03	23.24	30.28	46.48
Inanga	Niger Delta	NE	Nigeria	**NDE05**	3.79	1.44	0.41	8.08	1.32	1.37	1.14	1.14	1.13	13.45	1.05	0.61	0.38	0.37	0.32	0.97	26.82	24.01	49.16	0.50	0.51	0.51	0.01	20.25	30.68	49.07
Ubit	Niger Delta	NE	Nigeria	**NDE06**	2.71	1.37	0.57	4.11	1.62	1.68	1.13	1.14	1.12	14.19	0.83	0.57	0.36	0.45	0.41	0.66	30.92	29.23	39.85	0.43	0.46	0.45	0.04	23.55	31.77	44.69
Unam	Niger Delta	NE	Nigeria	**NDE07**	2.74	1.38	0.58	7.14	1.47	1.33	1.19	1.14	1.15	13.42	0.83	0.62	0.38	0.44	0.41	0.68	30.69	28.97	40.34	0.43	0.47	0.45	0.04	22.05	31.29	46.66
Yoho	Niger Delta	NE	Nigeria	**NDE08**	4.29	1.18	0.33	7.86	2.40	2.41	1.16	1.19	1.19	14.19	0.50	0.75	0.43	0.29	0.26	1.34	22.45	20.36	57.19	0.24	0.52	0.33	0.01	21.24	26.94	51.82
Dibi-6	Niger Delta	NW	Nigeria	**NDW09**	2.09	0.54	0.29	7.96	2.12	2.35	1.07	1.09	1.07	18.05	1.02	0.64	0.39	0.50	0.39	0.64	33.16	27.88	38.96	0.44	0.45	0.50	0.02	25.97	33.01	41.02
Dibi-11	Niger Delta	NW	Nigeria	**NDW10**	1.91	0.40	0.24	8.61	1.84	1.97	1.07	1.09	1.07	12.86	1.11	0.62	0.38	0.47	0.44	0.61	31.89	30.34	37.77	0.47	0.47	0.53	0.02	22.14	29.63	48.23
Gbokoda	Niger Delta	NW	Nigeria	**NDW11**	1.75	16.72	21.76	8.54	1.59	1.66	0.42	1.17	0.91	11.65	1.43	0.75	0.43	0.48	0.47	0.56	32.35	31.75	35.89	0.42	0.45	0.59	0.03	24.21	29.28	46.51
Malu-27h	Niger Delta	NW	Nigeria	**NDW12**	2.71	0.48	0.20	9.76	2.01	2.16	1.08	1.10	1.10	8.96	1.07	0.72	0.42	0.34	0.42	0.81	25.58	29.60	44.82	0.44	0.46	0.52	0.01	21.24	27.83	50.93
Malu-28	Niger Delta	NW	Nigeria	**NDW13**	2.16	0.78	0.42	10.86	1.52	1.57	1.08	1.11	1.07	13.07	1.05	0.55	0.35	0.46	0.36	0.73	31.40	26.37	42.23	0.43	0.45	0.51	0.02	22.19	32.68	45.13
Mer-12D	Niger Delta	NW	Nigeria	**NDW14**	1.77	2.53	1.69	9.48	1.78	1.57	1.33	1.12	1.23	14.78	1.10	0.57	0.36	0.46	0.36	0.73	31.39	26.51	42.10	0.48	0.48	0.52	0.03	22.08	30.81	47.11
Meren-14	Niger Delta	NW	Nigeria	**NDW15**	2.53	0.54	0.25	11.14	2.28	2.35	1.09	1.09	1.09	14.55	0.91	0.57	0.36	0.36	0.38	0.85	26.65	27.35	46.00	0.47	0.51	0.48	0.01	21.69	28.85	49.46
KC-W17	Niger Delta	Central	Nigeria	**NDC16**	3.20	1.00	0.35	0.86	5.87	6.77	1.08	1.12	1.11	15.00	0.80	0.56	0.36	0.43	0.39	0.73	29.96	27.99	42.05	0.44	0.42	0.45	0.02	23.83	28.67	47.49
KC-19t	Niger Delta	Central	Nigeria	**NDC17**	3.87	0.79	0.25	10.30	3.78	3.95	1.08	1.13	1.11	11.04	1.12	0.78	0.44	0.43	0.52	0.55	30.14	34.37	35.49	0.42	0.42	0.53	0.01	21.09	32.88	46.03
Oropouche	Ref. oil	Trinidad	Trin.& Tob	**TRO01**	1.59	0.46	0.33	8.16	2.36	2.50	0.98	1.03	1.00	19.23	0.95	0.84	0.46	0.52	0.48	0.50	34.36	32.47	33.17	0.44	0.48	0.49	0.34	24.70	36.61	38.68
Alba	Ref. oil	North Sea	UK	**NSA02**	1.01	19.71	6.26	2.07	13.25	2.11	0.40	0.41	0.30	31.57	1.80	1.17	0.54	0.47	0.45	0.59	32.12	30.92	36.96	0.54	0.59	0.64	0.58	29.77	28.79	41.44
Andrew	Ref. oil	North Sea	UK	**NSA03**	1.35	0.53	0.48	11.75	4.28	4.29	0.99	1.03	1.01	55.17	1.46	1.08	0.52	1.75	0.19	0.25	63.66	16.19	20.16	0.26	0.56	0.59	4.22	31.76	32.40	35.84
NSA-74	Ref. oil	North Sea	n/a	**NSA04**	1.29	0.54	0.49	10.71	4.01	4.09	0.93	1.00	0.95	54.66	1.87	1.27	0.56	2.09	0.20	0.18	67.66	16.79	15.55	0.24	0.54	0.65	3.02	34.94	33.78	31.28
Veslfrikk	Ref. oil	North Sea	Norway	**NSV05**	1.53	0.76	0.62	13.69	4.30	4.21	0.93	0.99	0.96	36.74	1.74	1.36	0.58	1.47	0.23	0.27	59.59	18.98	21.42	0.24	0.49	0.63	1.24	28.14	31.90	39.96

IIIb: Biomarker Parameter Data II

Terpane Ratios																								
Ts/Tm	BNH-I	29Hop	30Hop	31Hop	25Nor	NH/NM	Hop/Mor	Dia/NorM	D30/H30	29Ts/Tm	29Ts/30H	32H(S/R)	31H (S/S+R)	3H0/29H	HomoHop	35H/34H	Gam-I	Ol-Index	Ts/(Ts+Tm)	aaR29st/ab30H	%C31	%C32	%C33	%C34	%C35
0.68	1.54	0.43	0.89	0.30	0.40	1.36	2.05	1.47	0.69	1.52	0.97	1.05	0.56	1.56	0.59	1.01	0.17	0.85	0.40	0.53	35.67	24.22	21.55	9.23	9.33
0.45	0.00	0.43	0.88	0.31	0.08	2.91	5.19	0.67	0.15	0.32	0.20	1.27	0.59	1.57	0.49	0.47	0.04	0.24	0.31	0.14	53.09	25.87	11.39	6.55	3.10
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.26	0.17	0.26	0.89	0.48	0.10	4.53	6.43	2.02	0.19	0.49	0.22	1.39	0.56	2.30	1.20	1.05	0.10	0.12	0.56	1.12	35.11	25.07	18.42	10.47	10.95
0.69	0.00	0.34	1.03	0.31	0.11	2.48	5.02	0.58	0.12	0.61	0.30	1.38	0.53	2.00	0.53	0.00	0.05	0.40	0.41	0.17	51.51	24.37	13.01	11.11	0.00
0.70	0.00	0.37	1.05	0.28	0.09	4.00	5.03	0.88	0.12	0.47	0.25	1.34	0.55	1.90	0.47	0.50	0.03	0.31	0.41	0.10	52.40	24.38	14.38	5.89	2.96
0.60	0.00	0.26	1.28	0.30	0.44	0.64	3.73	0.00	0.00	1.36	0.51	1.54	0.47	2.68	0.35	0.00	0.14	0.55	0.38	0.28	62.84	19.62	17.54	0.00	0.00
0.67	0.00	0.36	1.05	0.29	0.11	4.05	4.52	0.88	0.11	0.32	0.16	1.33	0.55	1.95	0.51	0.62	0.03	0.30	0.40	0.14	50.09	24.13	15.12	6.57	4.09
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.64	1.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.57	0.00	0.00	0.00	0.83	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.72	0.00	1.22	0.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.82	0.00	0.00	0.00	0.81	0.42	0.00	0.00	0.00	0.00	0.00	0.00
0.66	0.12	0.52	0.89	0.23	0.16	6.36	5.15	0.45	0.05	0.29	0.21	1.37	0.56	1.37	0.43	0.35	0.04	1.33	0.40	0.02	47.83	25.31	15.39	8.51	2.96
0.68	0.17	0.52	0.92	0.22	0.20	6.05	5.10	0.71	0.08	0.20	0.15	1.35	0.57	1.40	0.41	0.60	0.03	1.60	0.41	0.01	48.03	24.78	14.34	8.00	4.84
0.74	0.20	0.62	0.77	0.23	0.27	5.81	4.23	0.75	0.11	0.32	0.28	1.35	0.57	1.14	0.44	0.55	0.04	1.88	0.43	0.01	46.23	24.27	16.02	8.71	4.78
0.73	0.12	0.52	0.87	0.24	0.15	5.92	4.98	0.65	0.08	0.31	0.23	1.38	0.57	1.37	0.46	0.45	0.03	1.19	0.42	0.02	47.56	24.95	15.17	8.48	3.84
0.71	0.26	0.56	0.92	0.19	0.32	7.13	4.96	0.80	0.08	0.21	0.16	1.39	0.55	1.33	0.36	0.82	0.02	1.74	0.41	0.00	47.84	23.70	14.88	7.45	6.13
0.61	0.12	0.56	0.82	0.24	0.17	4.87	5.09	0.50	0.08	0.26	0.21	1.30	0.57	1.26	0.47	0.51	0.03	1.16	0.38	0.02	44.93	25.06	15.54	9.61	4.87
0.77	0.16	0.58	0.81	0.23	0.33	4.88	4.36	0.62	0.10	0.30	0.25	1.27	0.57	1.22	0.48	0.56	0.04	1.53	0.44	0.02	43.56	23.73	16.21	10.60	5.90
0.63	0.24	0.62	0.93	0.16	0.43	7.57	4.85	1.12	0.12	0.31	0.25	1.30	0.55	1.26	0.28	0.00	0.01	2.05	0.39	0.00	52.23	28.52	13.34	5.91	0.00
1.17	0.00	0.43	0.99	0.25	0.07	5.32	6.78	0.58	0.07	0.31	0.19	1.41	0.58	1.65	0.53	0.60	0.05	0.50	0.54	0.01	43.02	26.89	16.52	8.50	5.07
0.99	0.05	0.40	0.96	0.29	0.07	5.10	5.63	0.69	0.08	0.30	0.18	1.28	0.57	1.70	0.61	0.55	0.05	0.42	0.50	0.01	43.30	25.99	18.27	8.04	4.40
1.10	0.07	0.46	0.89	0.27	0.07	5.82	6.05	0.62	0.07	0.30	0.20	1.35	0.55	1.49	0.56	0.65	0.07	0.45	0.52	0.02	44.30	27.51	16.15	7.28	4.76
0.81	0.22	0.63	0.84	0.19	0.27	5.42	4.87	0.74	0.12	0.29	0.24	1.29	0.56	1.18	0.36	0.51	0.02	1.23	0.45	0.01	46.51	26.06	15.84	7.68	3.91
0.93	0.00	0.54	0.83	0.24	0.30	4.03	4.87	0.61	0.12	0.32	0.25	1.39	0.56	1.30	0.51	0.68	0.07	0.71	0.48	0.01	42.89	25.59	15.43	9.58	6.52
0.90	0.00	0.53	0.82	0.26	0.42	4.02	4.35	0.72	0.14	0.40	0.31	1.34	0.55	1.31	0.54	0.72	0.11	0.72	0.47	0.02	42.19	25.53	16.49	9.21	6.59
1.04	0.17	0.63	0.85	0.18	0.41	5.15	4.81	0.70	0.11	0.29	0.25	1.29	0.56	1.19	0.38	0.54	0.05	1.54	0.51	0.01	44.79	24.99	13.15	11.07	6.01
0.83	0.09	0.58	0.94	0.17	0.16	5.69	5.49	0.65	0.09	0.24	0.18	1.30	0.56	1.33	0.31	0.37	0.03	1.01	0.45	0.01	50.75	25.67	13.29	7.49	2.80
0.70	0.09	0.59	0.95	0.17	0.15	6.44	5.39	0.77	0.09	0.27	0.20	1.27	0.56	1.31	0.29	0.46	0.02	0.98	0.41	0.01	51.50	25.80	13.84	6.05	2.81
0.83	0.21	0.41	0.91	0.30	0.13	4.82	5.03	1.13	0.14	0.33	0.20	1.37	0.56	1.64	0.66	0.89	0.16	0.17	0.45	0.18	40.25	24.20	17.75	9.43	8.37
1.36	0.29	0.33	0.68	0.53	0.24	5.12	5.09	1.90	0.23	0.52	0.32	1.47	0.56	1.63	1.60	1.14	0.09	0.11	0.58	0.27	28.50	24.57	19.58	12.76	14.59
2.37	0.04	0.21	0.86	0.57	0.04	15.56	6.41	12.09	0.29	0.87	0.33	1.29	0.56	2.65	1.84	0.92	0.08	0.06	0.70	2.03	27.40	25.39	24.63	11.74	10.85
2.27	0.03	0.22	0.81	0.59	0.05	0.00	5.93	0.00	0.25	0.79	0.31	1.46	0.57	2.49	1.65	0.99	0.08	0.00	0.69	1.33	31.51	26.42	18.68	11.78	11.61
1.72	0.00	0.27	0.95	0.43	0.23	6.66	7.58	2.72	0.18	0.46	0.20	1.48	0.56	2.28	1.15	0.86	0.05	0.00	0.63	0.53	33.68	25.19	22.01	10.27	8.85

IIIb: Biomarker Parameter Data III

Aromatic HC Ratios																	
2-EN/1-EN	MNR	DMNR	(2,6+2,7)/(1,4+2,3)D MN	236/(135+146)TMN	1,3,7/(1,3,7+1,2,5)T MN	MP(3+2/9+1)	MPI(1)	MPI(2)	Rc (Ro<1.35)	Rc (Ro>1.35)	MPR	4/1MDBT	3+2/1MDBT	1-MDBT/DBT	DBT/PHEN	%R(MDBT	3/2MB
0.77	1.68	2.39	0.85	4.35	0.53	0.35	0.49	0.68	0.69	2.01	2.41	18.74	1.21	0.32	0.27	1.67	1.98
1.51	2.28	12.05	2.15	1.53	0.68	1.28	0.94	0.94	0.96	1.74	1.55	18.52	3.57	0.29	0.01	1.67	10.64
3.04	2.33	14.72	2.83	1.99	0.86	1.06	0.98	1.03	0.99	1.71	1.32	2.60	2.60	1.18	0.01	1.15	21.28
1.87	1.43	5.61	1.83	1.01	0.68	0.76	0.79	0.70	0.87	1.83	0.84	11.19	1.08	0.50	0.01	1.54	3.70
3.18	1.62	6.12	2.69	1.57	0.66	1.62	1.67	1.90	1.40	1.30	2.26	0.27	4.41	3.74	0.03	0.56	11.78
1.94	2.06	10.43	1.65	1.14	0.55	0.58	0.46	0.53	0.68	2.02	0.89	0.00	0.00	0.00	0.02	0.00	26.87
1.30	0.83	4.06	0.96	0.76	0.74	0.79	0.54	0.57	0.72	1.98	1.06	0.67	1.16	1.18	0.18	0.80	1.27
2.56	1.57	9.45	1.52	1.22	0.56	0.54	0.52	0.58	0.71	1.99	0.87	0	0	0.00	0.04	0.00	20.88
0.00	1.79	13.34	2.01	1.07	0.54	1.01	0.71	0.74	0.83	1.87	1.43	10.02	1.94	0.35	0.09	1.51	20.61
0.00	1.62	2.53	1.80	0.75	0.65	1.02	0.49	0.51	0.69	2.01	1.42	13.09	1.68	0.13	0.06	1.58	13.78
2.55	2.15	15.01	2.54	1.41	0.66	0.94	0.78	0.76	0.87	1.83	1.35	16.40	1.26	0.30	0.04	1.64	39.03
2.39	2.00	11.19	2.05	1.51	0.66	1.03	0.96	0.94	0.98	1.72	1.26	14.43	1.45	0.46	0.01	1.60	15.25
1.21	1.91	8.44	2.58	1.15	0.66	0.92	0.81	0.87	0.89	1.81	1.05	0.72	1.08	0.97	0.13	0.82	12.08
1.58	1.63	8.32	2.60	17.14	0.62	1.01	0.92	1.00	0.95	1.75	1.25	0.88	1.08	0.77	0.17	0.87	10.83
1.86	1.84	6.56	3.03	0.91	0.67	0.98	0.82	0.89	0.89	1.81	1.18	0.63	1.16	0.68	0.17	0.78	13.14
1.29	1.49	4.71	2.51	0.78	0.55	0.84	0.75	0.80	0.85	1.85	0.97	1.04	0.97	0.68	0.24	0.91	17.04
1.04	1.28	5.18	2.38	0.92	0.59	0.90	0.87	0.92	0.92	1.78	1.05	1.02	1.12	0.66	0.25	0.91	12.90
1.09	2.01	6.12	2.83	0.90	0.57	0.76	0.75	0.82	0.85	1.85	0.83	1.32	1.17	0.61	0.27	0.98	8.64
2.42	1.57	7.78	2.58	0.95	0.58	0.94	0.89	0.90	0.93	1.77	1.14	0.75	1.00	1.00	0.10	0.83	14.34
1.41	1.94	8.01	3.30	0.97	0.67	0.85	0.81	0.96	0.89	1.81	0.94	0.00	0.00	0.00	0.00	0.00	14.74
1.30	1.82	7.59	3.17	14.58	0.61	0.81	0.77	0.86	0.86	1.84	0.98	12.49	0.77	0.12	0.07	1.57	14.01
2.53	1.95	9.78	2.45	1.18	0.66	0.95	0.88	0.88	0.93	1.77	1.23	15.34	1.87	0.27	0.02	1.62	3.34
2.95	2.11	18.25	2.25	1.99	0.64	1.10	1.06	1.03	1.04	1.66	1.45	3.99	1.96	0.77	0.04	1.27	18.58
1.79	1.49	6.42	3.09	0.76	0.62	0.95	0.96	1.07	0.97	1.73	1.29	0.80	1.50	0.79	0.18	0.84	5.36
1.05	2.45	9.79	2.96	1.36	0.72	1.02	0.95	1.02	0.97	1.73	1.36	7.47	4.21	0.23	0.03	1.43	10.95
1.37	2.33	12.20	3.25	1.30	0.67	1.03	0.87	0.93	0.92	1.78	1.30	0	0	0.00	0.02	0.00	25.57
1.30	1.48	8.50	2.44	1.43	0.63	1.19	0.90	0.93	0.94	1.76	1.46	15.13	1.43	0.10	0.03	1.62	50.71
0.00	2.40	25.24	1.98	3.86	0.61	1.21	1.11	1.13	1.06	1.64	1.49	1.32	1.42	1.55	0.03	0.98	35.16
3.35	2.74	18.13	2.23	2.00	0.78	1.28	1.14	0.97	1.08	1.62	1.33	0.27	1.43	1.71	0.04	0.56	19.96
0.00	1.58	5.21	1.04	1.01	0.61	0.67	0.72	0.72	0.83	1.87	1.13	0.19	1.58	1.76	0.22	0.47	7.91
2.89	2.07	11.98	1.90	1.45	0.75	0.74	0.84	0.87	0.90	1.80	0.88	0.74	1.52	2.07	0.02	0.82	8.02
4.16	1.59	6.27	2.42	0.99	0.77	0.73	0.62	0.61	0.77	1.93	0.90	0.09	2.24	1.07	0.07	0.28	5.53
2.82	1.75	9.76	1.79	0.78	0.62	0.77	0.71	0.75	0.83	1.87	0.92	0.50	1.20	1.63	0.02	0.72	9.95

MAS/TAS Ratios											
MAS21+22/tot	MAS29S/R	TAS/MAS	TAS20+21/tot	TAS21/(21+28)R	TAS28S/R	%TAS26	%TAS27	%TAS28	ST	MAS	TAS
0.08	1.07	0.73	0.26	0.22	1.17	0.06	0.25	0.67	169.50	0.00	0.00
0.09	0.47	12.06	0.17	0.19	1.08	0.09	0.32	0.65	30.28	0.00	0.03
0.39	1.94	37.65	2.99	0.86	1.32	0.41	0.26	0.44	20.71	0.00	0.05
0.18	1.60	11.98	0.45	0.56	0.82	0.15	0.50	0.35	152.28	0.00	0.01
0.12	0.61	0.21	0.15	0.22	0.84	0.08	0.31	0.56	8.86	0.09	0.02
0.15	1.27	16.71	0.05	0.10	1.37	0.09	0.32	0.57	187.09	0.00	0.01
0.17	1.19	15.70	0.12	0.32	2.23	0.02	0.48	0.41	354.39	0.00	0.00
0.09	1.21	13.09	0.03	0.08	1.43	0.12	0.39	0.51	271.59	0.00	0.00
0.00	0.00	0.00	0.00	0.00	1.33	0.29	0.29	0.71	0.00	0.00	0.00
0.06	1.98	145.88	0.10	0.21	1.28	0.28	0.32	0.57	0.00	0.01	145.9
0.91	0.00	30.24	2.78	0.76	1.00	0.40	0.40	0.60	0.00	0.03	30.24
0.10	1.66	11.36	0.16	0.21	0.89	0.22	0.36	0.44	16.63	0.00	0.05
0.08	1.62	110.93	0.12	0.21	1.14	0.22	0.37	0.45	75.96	0.00	0.01
0.05	1.76	50.61	0.09	0.14	1.18	0.20	0.37	0.45	96.61	0.00	0.01
0.06	1.75	113.18	0.11	0.20	1.11	0.24	0.38	0.42	87.78	0.00	0.01
0.08	1.49	356.11	0.09	0.15	1.23	0.17	0.32	0.51	33.29	0.00	0.03
0.05	1.73	45.83	0.07	0.14	1.04	0.25	0.37	0.42	163.50	0.00	0.01
0.04	1.71	41.51	0.06	0.11	1.15	0.24	0.39	0.43	161.69	0.00	0.01
0.05	1.51	0.77	0.15	0.15	1.08	0.12	0.35	0.54	4.25	0.12	0.09
0.06	1.31	294.78	0.16	0.24	1.10	0.22	0.35	0.43	25.20	0.00	0.04
0.06	1.36	195.99	0.11	0.19	1.06	0.25	0.37	0.42	36.50	0.00	0.03
0.06	1.69	10.93	0.18	0.26	0.97	0.22	0.35	0.45	75.04	0.00	0.01
0.13	1.30	178.06	0.22	0.24	0.93	0.20	0.34	0.48	6.83	0.00	0.15
0.08	1.69	21.05	0.12	0.21	1.11	0.25	0.36	0.43	56.13	0.00	0.02
0.06	1.63	61.77	0.17	0.28	1.07	0.24	0.38	0.42	100.39	0.00	0.01
0.09	1.54	208.00	0.22	0.33	1.19	0.23	0.36	0.45	36.20	0.00	0.03
0.08	1.73	218.74	0.22	0.29	1.23	0.17	0.34	0.48	148.11	0.00	0.01
0.10	1.28	139.24	0.32	0.29	1.00	0.22	0.33	0.50	12.14	0.00	0.08
0.14	1.79	115.17	0.61	0.54	0.79	0.20	0.43	0.39	24.21	0.00	0.04
0.10	1.00	5.15	0.32	0.44	0.89	0.20	0.44	0.39	168.35	0.00	0.00
0.50	1.38	109.17	0.57	0.60	1.16	0.15	0.47	0.39	44.62	0.00	0.02
0.41	0.94	17.18	0.13	0.39	1.91	0.23	0.44	0.39	796.55	0.00	0.00
0.37	1.29	85.46	0.17	0.37	1.47	0.16	0.39	0.48	70.61	0.00	0.01

IIIb: GC Peak Areas (*n*-alkanes)

GC Peak area (*n* -alkanes)																																			
Sample Name	Basin	Sample ID	nC8	nC9	nC10	nC11	nC12	nC13	nC14	nC15	nC16	nC17	Pristane	nC18	Phytane	nC19	nC20	nC21	nC22	nC23	nC24	nC25	nC26	nC27	nC28	nC29	nC30	nC31	nC32	nC33	nC34	nC35	nC36	GC-IntStd
Adgo	B/fort-Mackenzie	BMD01	597	17716	7398	241041	89666	111008	44607	87577	26212	13719	11415	30520	31683	15475	21423	1210	10560	1096	637	363	145	518	77	166	135	196	n.d	n.d	n.d	n.d	n.d	n.d	461756
Adlartok	B/fort-Mackenzie	BMD02	25718	29216	117615	162584	344181	921242	435703	340167	337246	324769	786642	190995	238507	148475	121201	71303	56991	42602	31242	23829	26130	15548	5895	7724	3246	3666	n.d	n.d	n.d	n.d	n.d	n.d	390832
Kugpik	B/fort-Mackenzie	BMD03	240305	514987	818934	956795	1129910	1341485	1315375	1403687	1216144	1148090	722226	1014516	434133	830063	821279	723817	681741	612657	546098	441115	357531	221022	145914	81736	51511	33529	14750	9361	4429	1280	n.d	405422
Mayogiak	B/fort-Mackenzie	BMD04	95245	62783	152556	139720	218896	325808	259641	294410	261515	248865	263791	188263	161568	174117	174998	163516	150747	135143	128805	107165	114134	69003	51684	45930	43553	35788	22166	17403	n.d	n.d	n.d	396114
Tarsiut	B/fort-Mackenzie	BMD05	13351	50821	172764	628903	709704	1052955	799686	762944	635013	555368	350761	456919	321062	332928	205911	115482	54921	26215	13979	6518	3623	3878	2614	1853	1489	1025	n.d	n.d	n.d	n.d	n.d	309684
ISS-0	B/fort-Mackenzie	CAN06	n.d	n.d	4141	28834	99386	216449	277113	392550	397121	363123	522472	318583	126518	294326	268232	229655	201986	179297	141424	123326	95071	82226	50385	48837	27484	47038	12763	10857	3814	n.d	n.d	136799
ISS-3	B/fort-Mackenzie	CAN07	n.d	n.d	36857	264402	282998	696574	657551	464193	182356	79915	347772	6412	68490	11990	14272	7813	3589	5107	1524	2717	6889	1810	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	248608
ISS-4	B/fort-Mackenzie	CAN08	n.d	3944	20077	39039	84658	148310	126630	169934	73500	72397	545161	10457	137409	49907	57702	41099	35667	34759	26087	27274	24971	21215	11168	13277	11261	43021	15612	4266	n.d	n.d	n.d	234474
Kut-aj	Kutei	KTM01	n.d	8746	436237	2165218	3850409	891879	3767108	2758920	1737825	1152544	1638768	687409	146121	408016	216397	116814	65029	37871	22285	13508	1895	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	358274
Kut-IJ	Kutei	KTM02	n.d	n.d	n.d	33402	176053	721015	2095606	6479571	6466830	3936707	942479	474803	91098	136283	117747	98896	88165	70577	59713	44717	45718	26517	18469	13018	9874	n.d	n.d	n.d	n.d	n.d	n.d	369135
Kut-v7	Kutei	KTM03	n.d	25837	371647	958761	1581738	1571439	2678555	2909939	2824672	2797320	3119254	2158270	512841	1898130	1654422	1401362	1135551	846250	568504	356808	221649	131104	68336	41043	20150	n.d	n.d	n.d	n.d	n.d	n.d	420521
Asasa	Niger Delta	NDE01	189243	136388	173776	259843	391359	665565	556688	614596	506916	460557	759366	378838	264454	349277	317240	291822	253833	243498	218548	192640	176435	155143	122972	117631	93151	125219	53838	56840	n.d	n.d	n.d	377892
Edop	Niger Delta	NDE02	n.d	91247	292589	339131	423185	506956	596906	672962	565947	487926	735699	452947	264198	407871	381127	376994	365610	362473	346504	344141	298515	291005	252343	265713	200087	190323	102169	82950	50873	26370	11624	674654
Eku	Niger Delta	NDE03	n.d	158526	364254	337599	393359	415670	506925	632749	544505	511441	776713	464109	257712	448548	437570	442087	436633	450989	434023	437609	400907	390573	323278	321708	238944	211384	109779	92041	47132	25530	10218	705988
Etim	Niger Delta	NDE04	n.d	232105	524373	560231	599225	579127	567768	570949	491690	449386	572759	392738	212548	364816	348160	335538	315899	306420	287779	287239	259462	258523	233197	234093	176904	173103	107076	89566	44229	31398	16236	623801
Inanga	Niger Delta	NDE05	n.d	284813	559598	607109	616098	602596	592710	617162	526326	493386	709401	458109	187210	432060	429120	423752	425076	425687	418459	417190	377662	373666	320038	313967	228819	219696	126464	116136	50579	38014	n.d	684836
Ubit	Niger Delta	NDE06	n.d	24728	115824	107687	210097	301074	384813	470143	412146	384623	527771	343382	195053	327178	313984	314724	301890	300619	283901	286007	240391	236896	199461	192467	140092	127871	78344	64705	29862	21543	943	573255
Unam	Niger Delta	NDE07	n.d	209461	424840	449665	504846	507916	540224	614577	534072	512127	704229	440470	256773	415358	394753	401699	385609	384063	372903	381314	336440	348625	323004	355436	276061	267784	159670	135795	76125	46443	22949	797177
Yoho	Niger Delta	NDE08	247379	482046	626678	631372	698155	922866	792920	823246	727569	681421	802466	567306	187196	534285	500672	468594	435747	410875	375823	348763	315044	283597	229972	224812	156545	206057	87321	83595	33136	22108	n.d	325427
Dibi-6	Niger Delta	NDW09	n.d	39490	182609	288381	337637	343538	348435	358546	326319	316512	169558	282315	81208	271030	259254	250471	229411	218769	200376	189823	161975	149465	119347	101375	70462	53957	33808	22264	11240	6346	n.d	580250
Dibi-11	Niger Delta	NDW10	n.d	315616	767596	899424	921719	909015	887333	902503	842491	765057	305949	655492	160530	643971	611514	590459	561760	550416	514489	493597	434097	416339	336198	297345	219638	173242	113108	79851	43543	27487	n.d	653383
Gbokoda	Niger Delta	NDW11	12891	16351	24620	19181	56607	277763	72600	41501	10068	34047	569196	14933	324977	21398	2602	38241	8204	10707	19129	25204	8332	21417	13335	7622	22762	64307	68413	30986	10849	n.d	n.d	418222
Malu-27h	Niger Delta	NDW12	380	861	1164	1192	1167	1254	1070	1036	912	834	399	740	147	682	643	610	577	554	515	496	449	416	333	295	211	206	119	85	56	28	20	298
Malu-28	Niger Delta	NDW13	n.d	358783	652545	630681	523080	467918	419312	424367	339989	311826	242724	267317	112468	254113	244970	241035	230304	234308	223487	227189	203169	205522	166756	158712	126783	103072	61201	45731	22787	13965	8178	621002
Mer-12D	Niger Delta	NDW14	n.d	36833	108366	140404	144077	152517	172367	149636	134800	97634	246956	82519	139866	75878	72274	75961	60486	61799	62229	66092	56164	54705	45161	63662	50786	35689	22282	11898	10198	8621	n.d	623634
Meren-14	Niger Delta	NDW15	n.d	384262	799710	911117	988623	931117	891419	865647	715091	624717	335540	532964	132398	481858	438876	416796	385259	369167	347189	324875	285916	273992	221758	201633	146644	115592	71879	53821	32446	18421	n.d	533674
KC-W17	Niger Delta	NDC16	n.d	9657	37329	82537	132220	388646	986498	1710526	1869286	1819671	1820716	1622633	569677	1363916	1145691	960463	828432	713438	596820	493940	382051	310020	222588	177099	104539	85724	40880	27465	12919	7055	n.d	681980
KC-19t	Niger Delta	NDC17	18	82	173	246	286	356	293	287	242	218	172	179	45	160	140	126	110	98	85	76	66	58	44	39	28	31	15	11	5	n.d	n.d	63
Oropouche	Ref. oil	TRO01	22	90	141	157	188	269	197	186	180	166	76	147	48	139	134	137	116	106	99	90	82	70	61	49	39	35	22	12	8	5	n.d	79
Alba	Ref. oil	NSA02	n.d		19	2	3	18	13	21	7	4	84	13	84	24	8	4	0	0	1	11	11	0	14	5	11		25	12	13	7	2	342
Andrew	Ref. oil	NSA03	386	64328	234461	322520	339622	439834	309700	278194	241567	216632	114228	174451	84434	155351	143540	120188	105744	91823	84555	73225	65169	50629	42359	34529	27086	21381	14123	6610	n.d	n.d	n.d	137845
NSA-74	Ref. oil	NSA04	4417	115154	295848	367647	398522	528101	393313	350360	322786	277760	150865	238844	116553	202209	196213	161046	142978	126261	116480	106972	89501	69305	60569	45840	38201	30303	20687	9973	9217	4604	n.d	167467
Veslfrikk	Ref. oil	NSV05	5465	154671	321600	340760	339385	401645	282903	269834	207648	182399	138478	145517	90325	125669	117520	95263	83760	3335	68689	59931	53187	42435	36318	29111	26160	23514	15983	11060	11537	7156	n.d	152516

IIIb: GC-MS Peak Areas (Steranes)

			GC-MS Peak Area (Steranes)																				
Sample Name	**Basin**	**Sample ID**	**St27dbS**	**St27dbR**	**St28dbS(1)**	**St28dbS(2)**	**St28dbR(1)**	**St28dbR(2)**	**St27aaS**	**St27bbR**	**St29dbS**	**St27bbS**	**St27aaR**	**St29dbR**	**St28aaS**	**St28bbR**	**St28bbS**	**St28aaR**	**St29aaS**	**St29bbR**	**St29bbS**	**St29aaR**	**#217 max**	**St-IntStd**
Adgo	Beaufort-Mackenzie	BMD01	52436	34681	31230	46373	20483	20949	43704	222674	200163	71569	211650	188735	29600	94676	192746	103474	271150	222707	187462	290306	221535	6905393
Adlartok	Beaufort-Mackenzie	BMD02	20727	13385	6462	12853	5593	14186	13669	67265	65604	21598	64179	56968	n.d	21722	23412	17300	59365	54885	28243	69469	69627	4540260
Kugpik	Beaufort-Mackenzie	BMD03	42127	28365	27715	30368	19659	15739	n.d	26318	41789	13815	n.d	32677	n.d	17832	19713	n.d	n.d	19022	16565	n.d	41045	2793005
Mayogiak	Beaufort-Mackenzie	BMD04	203266	135153	155069	166682	102182	87617	125679	252966	213314	289755	105055	180123	144148	167931	212816	124074	167562	157949	160404	137393	207328	8516129
Tarsiut	Beaufort-Mackenzie	BMD05	23249	10788	13738	13718	10886	12576	4434	21841	28493	14235	10464	27458	31109	13347	23104	34107	43739	46084	24905	68146	78477	4978823
ISS-0	Beaufort-Mackenzie	CAN06	57363	43395	50549	52986	24769	39658	33929	136436	144223	63946	135305	105504	67485	53619	73450	78258	145252	108893	79916	230528	191676	5457432
ISS-3	Beaufort-Mackenzie	CAN07	n.d	n.d	n.d	n.d	n.d	n.d	3492	7993	n.d	6230	6913	n.d	n.d	5850	5086	10732	8275	15708	n.d	33212	31895	11221245
ISS-4	Beaufort-Mackenzie	CAN08	133189	84095	96095	107352	64908	73468	69066	260161	205932	144424	273190	154922	140766	119646	166250	193880	313935	303513	192462	417150	403894	11038483
Kut-aj	Kutei	KTM01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0	2053463
Kut-IJ	Kutei	KTM02	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0	2174459
Kut-v7	Kutei	KTM03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	6174	2480377
Asasa	Niger Delta	NDE01	35639	26335	23870	33913	10841	19346	53986	71765	75033	44130	72408	49385	66545	53200	55646	62572	90126	72074	51189	104571	90395	4323049
Edop	Niger Delta	NDE02	123350	77253	80119	121079		168054	263520	257620	249337	233369	264543	226080	318320	195480	234051	250315	357502	358435	196630	418600	336751	107515186
Eku	Niger Delta	NDE03	188114	108424	89185	151983	47352	81542	319914	311092	301230	195406	313798	294917	335150	355406	280409	306637	513310	449659	224200	517704	508452	109476048
Etim	Niger Delta	NDE04	151164	83270	66530	125935		113014	276061	254983	244458	201693	297019	224360	267329	208742	224375	290911	393393	332401	207653	379617	411771	112981603
Inanga	Niger Delta	NDE05	68231	35730	39588	57004		60934	109241	120858	130244	63790	110680	121728	103341	61099	79591	99085	212893	159219	93837	202855	160458	107189767
Ubit	Niger Delta	NDE06	194034	129743	103763	153942	52209	126914	403553	351138	314177	249554	527980	300308	422448	405763	287394	499197	567105	464198	245565	680457	711563	111916938
Unam	Niger Delta	NDE07	211266	104009	111244	160727	52709	122658	397726	363297	350036	228884	523020	317205	441739	426810	288375	493804	570976	513800	260913	687454	680017	98376816
Yoho	Niger Delta	NDE08	20851	10256	10917	14569	6221	7756	8874	39416	46605	19608	28211	29310	27971	15150	24385	25586	35739	45885	34668	71876	75598	5399948
Dibi-6	Niger Delta	NDW09	62191	34776	33686	39119		50432	89188	80140	88256	69256	113459	64891	78373	65391	73301	95417	135383	111125	60504	133327	111242	99753254
Dibi-11	Niger Delta	NDW10	67191	39641	32172	55088		55756	155205	141072	134684	111819	178479	98094	153056	122928	104135	169820	235488	179082	98095	211383	202326	96011988
Gbokoda	Niger Delta	NDW11	40444	27848	21935	32191	10041	18426	80279	88828	84786	62177	109927	46422	87266	87497	77648	107892	174899	111543	109708	121948	132170	4575074
Malu-27h	Niger Delta	NDW12	16244	9391	9682	14168	4281	5457	33324	45494	38485	34126	41797	22984	41872	39424	36573	48375	78140	68318	40652	73256	71453	6445323
Malu-28	Niger Delta	NDW13	100174	63365	56177	90319		94411	193764	199377	175307	162701	254401	157352	175301	184013	158493	213681	360769	228701	155713	342111	262474	114119362
Mer-12D	Niger Delta	NDW14	173987	115145	85186	171727		146468	349464	318751	299607	254396	376368	317343	290261	352652	255194	317865	553743	398051	210245	504808	463293	95528942
Meren-14	Niger Delta	NDW15	81281	50052	40693	69937	24094	39951	133613	146850	148121	88923	148966	151300	156719	159112	108391	152916	234338	194039	86015	257134	211687	97410186
KC-W17	Niger Delta	NDC16	100714	75332	58504	78672		74609	196518	196434	174420	116371	253336	176404	173151	212360	147684	236658	285254	237720	119464	355530	404695	108122702
KC-19t	Niger Delta	NDC17	14864	9576	7696	14232	5745	10435	31936	35946	30588	27218	44433	22757	36641	36672	28388	50659	58410	58287	27948	52308	57768	5756147
Oropouche	Ref. oil	TRO01	55468	34333	31291	48910	24191	28714	84372	96631	90581	96532	108904	50052	95568	109176	93590	102918	99424	93849	78751	105141	105843	7252981
Alba	Ref. oil	NSA02	482333	324405	221147	259182	155909	144159	292939	671753	638419	498294	250529	484701	343342	314952	387176	241156	519116	517156	423929	288314	665460	24505416
Andrew	Ref. oil	NSA03	68505	52938	36928	41435	22513	23031	21550	59634	80260	45441	60872	56774	19705	20227	30856	15477	28128	27883	23382	19274	65163	5795398
NSA-74	Ref. oil	NSA04	95030	59257	50905	44102	25869	28294	27159	87645	89930	57561	85391	48224	25369	29378	44725	21190	36677	41727	29953	19625	105888	7852163
Veslfrikk	Ref. oil	NSV05	60008	38274	32219	40647	18284	20275	23545	77035	80534	50830	72711	59053	22144	32814	46445	23163	45471	56479	41163	26138	81817	7326365

IIIb: GC-MS Peak Areas (Terpanes)

GC-MS Peak Area (Terpanes)																										
Sample ID	T27N	T27H	T28nH	T29nH	29H (C29Tm	T29N(C29Ts	T30D	T29M	T30O	T30H	T30M	T31HS	T31HR	T30G	T31M	T32HS	T32HR	T32M	T33HS	T33HR	T34HS	T34HR	T35HS	T35HR	#191 max	Tt-IntStd
BMD01	183602	270681	619961	160910	259218	393238	279718	190453	343576	403699	197029	110558	85615	69369	96966	68219	65004	42950	74469	44064	29860	20920	51290		583697	6905393
BMD02	45558	100184		30139	235262	74272	54551	80977	89720	369030	71049	109319	75143	16222	33491	50231	39672		25097	14468	9684	13078	10778		179575	4540260
BMD03																									19932	2793005
BMD04	104422	82773	74183	43392	189070	93578	84179	41694	51523	433931	67475	166052	131065	43788	59164	123462	88659	52639	93091	62754	55463	33108	52021	40605	130310	8516129
BMD05	40764	59508		32495	143024	86992	33464	57583	114490	286368	57096	71690	62894	13941	32901	36876	26798	16889	21967	12015	18215	10823			179201	4978823
CAN06	193352	276600		123393	746367	347842	164360	186438	437020	1415511	281606	332473	268326	38645	114797	160311	119198	41230	95832	68993	36621	30915	22902	10986	528550	5457432
CAN07	8729	14439		12432	10635	14492		16658	15747	28551	7646	5474	6204	4083	4960	2210	1437	3117	2136	1124					164274	11221245
CAN08	318210	472410		269814	1270492	402191	277349	313493	739091	2479887	548150	601332	485000	73888	227163	298509	224794	84143	191177	136846	78716	63718	58027	30778	863187	11038483
KTM01																									0	2053463
KTM02					12217				15907	19204															0	2174459
KTM03	5872	8160			17651				11677	14457															33822	2480377
NDE01	123114	185743	137994	174705	806925	237942	57587	126789	1472339	1109197	215513	240406	192637	44082	81505	132617	96499	67201	83650	55699	48031	28992	26780		786624	4323049
NDE02	644447	943218	865537	1033318	3717511	759002	437001	614066	8311331	5207399	1021238	1107745	852051	156526	328854	581387	429919	150660	339100	246209	200512	126024	105602	91919	8342133	107515186
NDE03	792875	1071391	1134098	1532304	4963170	1604174	642154	853760	10589672	5635988	1332741	1378145	1022503	226239	338046	724802	535408	238732	507930	323755	274806	177556	134153	113870	10615794	109476048
NDE04	554114	757856	485679	616834	3015257	941728	329862	509703	4916781	4125422	827768	979930	741584	137380	246609	524136	379088	194531	320106	228863	190506	116583	80688	58427	4914624	112981603
NDE05	382249	541722	880274	1109571	2588489	555015	292090	363044	6009936	3447969	695436	633079	509015	77970	191911	329346	236500	144950	209491	145650	107194	70707	69669	76693	5984151	107189767
NDE06	669118	1102175	671462	947132	4394607	1160043	449861	901704	6460341	5550529	1090304	1340364	1006552	186827	352237	739230	569561	225197	458851	352630	304597	197368	143037	111368	6494720	111916938
NDE07	720371	930646	810224	1654551	4148515	1258965	524286	850083	7768850	5064021	1161668	1222290	907211	217580	352705	648821	511225	268761	459170	333190	300664	217753	148658	139914	7751754	98376816
NDE08	195438	309188	405544	727375	1346952	421592	199984	177897	3499718	1703861	351235	266651	217777	23417	71584	149349	115217	52536	77867	45847	34046	20736			1264289	5399948
NDW09	265154	226061		119747	973566	304900	105757	182937	796279	1608181	237200	374350	270441	74292	68023	235632	167391	128030	143230	104284	77575	49846	43721	32221	1665896	99753254
NDW10	436982	439185	153974	193032	1729413	524568	235413	339177	1234082	2939183	522030	768961	570992	136334	205889	450750	353364	119035	329367	235857	143317	105618	79030	57254	2683701	96011988
NDW11	259263	235889	126963	122118	1204603	366299	127874	206959	809157	1798421	297292	444429	360579	124285	133627	287532	212401	74252	173928	119587	84556	47829	47311	39101	1115045	4575074
NDW12	189295	232761	242623	298813	926402	264788	126384	171052	1341622	1090111	223945	208939	164581	16642	51557	117851	91473	29697	72265	54953	36723	24976	18330	13047	1354969	6445323
NDW13	713877	766991		1162297	3003343	964743	457827	745027	2760709	3900386	801212	934095	745556	292526	262426	582751	419398	211920	355187	248934	225564	149447	138289	117117	3873221	114119362
NDW14	1109774	1228964		2202531	4027929	1620167	725463	1002743	3785764	5274204	1212343	1318378	1061506	554787	529131	824748	615412	436557	586484	343680	314757	204660	195164	176575	5270612	95528942
NDW15	541375	522326	521180	1237278	2546956	748390	348553	494985	4682697	3039962	631921	579509	453960	140704	146868	324527	252073	156395	185557	117833	147502	107973	66691	71968	4705873	97410186
NDC16	584741	705094	402784	697557	3211227	780682	366739	564064	4315395	4255974	775631	730712	573329	127454	195625	372510	287200	158229	201744	139640	116115	76418	40923	31005	4239463	108122702
NDC17	130638	186392	84179	138670	686821	183989	81744	106591	879278	899536	166973	146343	116881	17794	53683	73881	57973	27015	41201	29525	19347	11586	9746	4625	874849	5756147
TRO01	62908	75926	75316	46636	214401	69916	50089	44471	60093	350600	69683	95519	74295	57639	79941	59105	43003	48193	45075	29793	23767	16038	16020	19276	337649	7252981
NSA02	500581	367827	405429	332450	844525	439841	313788	165017	150725	1378238	270833	661632	516456	117507	179441	604155	411605	181319	463743	345765	311209	216061	370913	231992	1452321	24505416
NSA03	26465	11152	2852	2692	23986	20952	18637	1542	3655	63572	9915	27904	21785	4852	10241	25962	20086	17374	26712	17948	12227	9058	11419	8252	23940	5795398
NSA04	46656	20574	3134	5626	43245	33973	26865			107893	18202	50789	38590	8924	17081	44493	30448	18250	33215	19778	22133	11295	18782	14154	41657	7852163
NSV05	46592	27066		43903	85416	39615	34810	12820		194438	25638	66900	52262	9838	24210	53226	35900	19573	47061	30803	22788	13566	19481	11837	57232	7326365

IIIb: GC-MS Peak Areas (Aromatics)

GC-MS Peak Area (Aromatics)																							
Sample ID	Naphthalene	2-MeNaphth	1-MeNaphth	2_6+2_7 DMN	1_5 DMN	Phen	3MePhen	2MePhen	9MePhen	1MePhen	DBT	4MDBT	3+2MDBT	1MDBT	Biphen154	MeBiphen1	MeBiphen1	MeBiphen1	Arom-IntStd	2-EN	1-EN	1,3+1,7-DMN	1,6-DMN	1,4+2,3-DMN	1,2-DMN
BMD01	13574	11048	6570	16377	6846	299537	561080	1247536	4721467	517148	81966	490434	31672	26165	8507	11511	22770	7795	81580468	0.0220956	0.0287159	19774	19248	19295	12327
BMD02	405737	3612573	1584382	8376329	695153	9435559	5734305	5780815	5247803	3734510	132579	711028	136885	38385	4416962	1847249	19659251	7613118	92048394	1.0647312	0.7063908	9027362	4568985	3891101	1316270
BMD03	180801	1570711	673771	5465030	371343	13642075	10926684	12134002	12538111	9196645	79690	243782	243856	93637	7575984	928347	19759310	8531424	106020451	1.134355	0.3735086	4723341	2663631	1928130	516277
BMD04	74018	681474	476784	1678067	299332	3913934	3695772	2958242	5270479	3504677	42803	239410	23202	21401	2966227	1826501	6753928	2589039	104730903	0.6031957	0.3232734	2386810	1493870	917464	422820
BMD05	12271	40716	25104	77779	12702	8857653	13433242	17766161	11382875	7855601	283623	286876	4678675	1060533	35504	6384	75172	45557	180764286	0.0536785	0.0168638	78052	53149	28935	14557
CAN06	16228	33698	16348	344233	33007	2225155	629932	834893	1576313	934619	55151	379918	472625	0	417498	185233	4977458	1618270	79643959	0.0208087	0.0107213	394828	230130	209185	65059
CAN07	65870	377623	453347	1304814	321503	494739	152617	173172	249409	163566	91484	72025	124570	107775	455326	814398	1037119	535765	160331258	0.3913997	0.3007712	3150778	954458	1365570	318514
CAN08	23675	116174	74151	381147	40324	2310025	944676	1222092	2586459	1404530	100539	458566	652596		382319	235136	4910528	1485957	153258602	0.0812946	0.0316945	448752	284939	251137	73262
KTM01	14467	1459217	815661	6034423	452325	829700	358221	389522	469445	272557	76813	268363	52022	26789	4789890	724408	14926992	4216134	104838077	0.5736729	0	6113987	10520396	2999973	1252779
KTM02	9533	126736	78321	1320370	520989	2520822	575236	625738	731359	440874	145681	242696	31123	18536	2201313	216539	2983576	1374897	91048186	0.3213063	0	1784443	1788435	732542	504807
KTM03	1091012	8124435	3781058	16464576	1097115	6593436	3878382	3678141	5272777	2727331	237820	1181668	90774	72044	6548207	829635	32380330	10185518	106871292	2.9187984	1.1447825	15567221	20913108	6487925	2203479
NDE01	352827	2347102	1175102	4855182	433993	3606326	3077802	2982176	3500931	2360395	52300	343664	34656	23819	1124326	218252	3328310	1226269	95935475	1.3337244	0.5588151	5013977	3511231	2373638	852033
NDE02	1044790	12248314	6426684	34436771	4078348	6189428	3745354	4355970	4654143	4140146	818938	567645	857346	790752	2598281	468793	5661178	2251665	103682399	4.4573685	3.6714462	33062590	25035270	13326835	5709918
NDE03	461247	9700722	5962715	27965892	3360111	5844124	4160273	4915158	5016206	3941290	968207	657853	801890	744052	4284853	314866	3411318	1360836	113116416	4.9130883	3.1078609	26744738	22769546	10745794	3939206
NDE04	11148648	73071062	39793481	59993457	9147220	6281676	3594489	4212766	4400809	3563267	1093438	468534	856848	740003	2645805	412099	5414009	2288744	103771379	37.581266	20.253274	62681163	54895026	19792959	8461618
NDE05	500063	6773988	4552245	14634442	3104605	1772124	1016045	1168171	1381638	1206513	422179	298546	277800	286000	225202	136819	2331123	782221	113904970	5.1975654	4.0176193	19038251	15365119	5840362	3285231
NDE06	102256	4143705	3235571	17704943	3416642	2864338	2147367	2444740	2755944	2323103	703183	478082	524324	466965	511827	161545	2084125	789587	100481083	3.6995861	3.5726465	20783005	18317056	7435719	3789583
NDE07	1203539	12665154	6309931	22699657	3706079	2154182	1392867	1724834	2040825	2080890	589252	471325	417812	357761	467895	204972	1770081	604782	103661837	5.4578187	5.0236885	23649426	21815798	8034955	4410629
NDE08	8881559	18848694	11982726	14791210	1902094	3105353	2458357	2519686	3079154	2204801	302456	225500	302919	301729	1314930	225634	3236642	1128698	152153018	12.411155	5.1321592	15386902	11703302	5728766	2420215
NDW09	599684	8144425	4191269	22065750	2756013	3347203	2018525	2927267	2697614	3106969	118000	251850			2387696	386789	5702851	2323276	115773531	3.293286	2.3303833	20978997	16850217	6686956	2816833
NDW10	1701796	13900145	7642724	27453168	3617234	3356565	2072276	2595589	3098633	2645055	243407	375292	23291	30058	2822832	535915	7508685	3009868	118523275	4.9321249	3.7999675	25881194	21679675	8666701	4190680
NDW11	1682759	6846734	3503788	11973733	1224208	4555965	3545471	3526726	4582116	2873887	73990	309368	37741	20163	786673	450218	1504564	691098	49309143	9.3826133	3.7084123	12570897	9050258	4878004	1775850
NDW12	1861249	8524942	4038981	16716118	915909	8675768	8771354	8265045	9724750	5700635	353198	1086393	532852	272207	6236969	1245903	23150213	8317418	246469338	1.8686722	0.6339194	15320211	9982230	7439140	2317028
NDW13	2005148	11774831	7900557	28995669	4513504	3834741	3250050	4112530	4532220	3194437	675607	427357	803231	535289	536912	329977	1767053	882656	98932651	22.320948	12.444927	26754050	17427144	9368705	3812621
NDW14	2397848	17435473	7114848	45612016	4661327	14935976	11245104	13231967	14180986	9718222	433851	739001	416857	98965	3398271	770568	8439581	4280909	102703058	7.1964744	6.8553024	35800644	23041111	15403560	5475858
NDW15	15047564	71299453	30581782	105861757	8677925	21596749	13556318	15288191	16158136	11726983	426770	975236	98989		15232237	1125988	28789839	11723616	127996591	6.1319989	4.4799703	83022370	59331776	32552025	12391036
NDC16	3224563	7340410	4956091	53457425	6288466	29346718	16963430	18238155	17085359	12520147	805999	1268267	119563	83849	8968673	992448	50331541	17715433	108749282	12.264683	9.4176231	51055633	36826089	21925701	7798346
NDC17	114368	718071	299119	3387626	134238	14124760	13095324	13638644	12988197	9162889	452733	925415	998797	701841	6473233	887004	31184804	13140947	177390275	0	0.1535646	2896773	1705268	1708682	462541
TRO01	231055	3486680	1271143	14405220	794423	39504129	41721799	31220305	33333322	23481145	1660387	772614	4059564	2838988	22583189	2538491	50660364	21959574	162054041	0.5932741	0.1769639	12125273	6966038	6448039	1793684
NSA02	33067	39033	24759	585842	112488	16099603	13765396	13736571	29237238	12114062	3550275	1210239	9864891	6248809	216971	218631	1729786	878782	159221844	0	0	856661	450763	565947	282276
NSA03	35225	222327	107182	1103878	92126	5976370	6639281	7118622	10575068	8116289	130666	199960	410160	269872	2881142	1041502	8350077	3886168	79131016	0.0642118	0.0222199	1061416	714586	582284	178299
NSA04	4507105	21418096	13505400	32168986	5126963	38535041	18828724	18286538	30650439	20310052	2846316	284027	6832206	3054235	26806249	5029922	27811856	10639163	76439389	10.384555	2.4972058	37210957	25091741	13320127	4710380
NSV05	780515	3136761	1791727	4459906	457175	14566580	8534704	9466482	13185616	10304375	293856	239719	575995	478262	11550917	1962951	19537685	6956879	134806463	0.9882602	0.3502381	5044069	3547512	2491623	792670

IIIb: GC-MS Peak Areas (Aromatics Cont'd)

GC-MS Peak Area (Aromatics)																									
Sample ID	1,3,7-TMN	1,3,6-TMN	1,6+1,3,5-TM	2,3,6-DMN	+1,6,7+1,2,6-	1,2,4-TMN	1,2,5-TMN	1,2,3-TMN	Fluorene	3-MF	2-MF	1-MF	4-MF	4,6-DMDBT	2,4 +2,6-DMDBT	1,4-DMDBT	1,3-DMDBT	3,6-MP+(2+3+	2,6+35 DMP	2,7-DMP	3,10+1,3+2,10+3,9-	1,6+2,5+2,9-DMP	1,7-DMP	2,3-DMP	1,9+4,9+4,10-DMP	1,8-DMP
BMD01	46843	28436	44616	193906	93836	59670	42186	121296	216184	178426	121325	555791	724942	248026	30558	21559	63113	5584408	2005875	4847832	21871881	6865705	3189811	4606798	4243175	352681
BMD02	9097693	9129325	6917550	10568363	16253831	815290	4235359	1163191	7785173	3198546	3697069	9963872	1399207	423382	224375	27075	66546	2683937	3292691	1656546	7602903	3691549	3038128	1371796	1197569	494787
BMD03	6258147	7092121	3926009	7816845	7531858	323602	1011054	377950	4069395	2278197	2985398	6156285	1035295	488866	439216	118564	111193	4028285	5612428	3231478	20678594	9838799	6514238	3046973	4013640	1625717
BMD04	2155215	3442592	2568380	2584479	5143102	239660	1000310	383475	3453250	1997905	1847985	5093122	1232042	74735	30529	22015	11581	1988577	1602843	886690	8867538	3553558	2424223	978664	2073472	923524
BMD05	75291	86467	77334	121255	239982	13454	39256	23505	2493727	3108084	4378492	9926191	1881784	9486027	9810372	2276772	2535602	6435011	10850587	6411465	21347664	10024671	6266687	5146816	2575770	1208064
CAN06	816746	1128047	626675	714179	2207411	76401	658682	156114	3177334	1385944	1062064	3995609	513815	107397	55663	n.d	n.d	558743	502314	323599	2981587	967656	1047846	476144	588297	493020
CAN07	3761538	3019723	2548833	1931026	5714949	198451	1354271	288212	436836	n.d	281680	374307	107895	33501	42601	18815	7950	90038	41864	30504	271296	99979	94580	33169	52221	44994
CAN08	952506	1385215	720000	877167	2853105	96769	743843	245801	3717873	1495398	1093250	4700925	813155	168814	73387	45116	29841	827412	682990	363503	2378991	1221124	1306592	394706	533891	659649
KTM01	5244653	6851483	5420693	5783552	19771604	443352	4476883	617401	866355	289894	308261	1607728	162912	90073	41495	16081	13207	111562	132674	56485	464330	223322	151793	63883	60055	28503
KTM02	10220868	16607172	14841446	11202963	20220852	1340539	5391694	1021615	5753601	3247090	3525998	1.1E+07	2440096	63587	30115	4991	9079	261007	327733	165085	1007355	488550	418750	169756	158684	58784
KTM03	15435048	18636470	13197234	18595898	41883113	1039373	7847817	1538918	3732326	2271527	2360406	1.1E+07	1153056	466272	116252	65985	55222	2325686	2842544	1164922	8105209	4267275	2534431	1492217	1160084	548720
NDE01	3987464	5321474	3683918	5545494	8961061	420283	2030669	593798	2405024	1470745	1405869	4603425	752200	113532	75510	10535	18616	1491489	1668068	885365	7054233	3101266	2924696	1047330	1003648	415458
NDE02	20350179	30475603	19865925	22760211	38922509	2329252	10671675	2127263	3123020	1449352	1698015	5247044	1135950	538891	1137942	629975	299428	1964655	1810193	1093579	8114272	4034188	3656542	1271731	1850598	792786
NDE03	17895350	27486220	1071821	18375140	35558795	2283675	10827308	2142659	2850227	1408786	1677704	4460625	1081882	548878	1210686	600025	291681	2048247	1819061	1200804	8431438	4267956	4302516	1337678	1786314	862772
NDE04	20888791	32578215	22532128	20488445	34330627	2602345	10481511	2084030	2843089	1199876	1551317	4560767	1015913	459981	1127962	515918	226358	1805022	1638029	1067993	7577977	3801577	3392140	1202189	1742317	861886
NDE05	9095550	15189487	10148450	7867311	19488857	1256289	7406191	1154799	673288	340378	445151	1411225	311794	344944	416953	198009	103892	673632	671586	453671	2985498	1666362	1594952	556500	800500	373035
NDE06	12377500	20455412	14245248	13078516	24553470	1780599	8570315	1595641	1311055	686050	884011	2904516	662475	420601	765786	384587	182404	1237131	1070639	677105	5249924	2814463	2605235	899678	1239167	621684
NDE07	10740035	18206921	12332667	11110685	22484772	1612306	8044285	1326164	1354110	596453	744232	2408455	556589	297528	512529	264612	128557	906529	737724	458242	3694638	1901179	2204475	659205	810954	376410
NDE08	5786900	8330973	5985542	5710877	11153533	907525	4189501	781065	1126431	707086	821195	3726859	392516	234318	326837	170201	115630	1300054	1574355	871059	5634405	2767618	2991771	1040015	1079424	528389
NDW09	11831366	17826152	11912807	11499568	19271825	1274223	5958773	1351662	1024550	550016	898406	2815915	594387	n.d	n.d	n.d	n.d	981241	820057	965143	4712579	2698392	2296119	647450	1435640	491886
NDW10	13761045	21406784	978117	14261278	24106565	1640782	8829669	1445698	1054237	514434	742451	2630529	525341	133921	25158	n.d	n.d	1067945	986969	701746	5378846	2655313	2206994	857765	1383522	593440
NDW11	8158659	10191572	7684172	9044542	14203047	707687	4163440	828153	1219663	1087240	1119039	4643695	630194	132142	90037	29747	43097	1355956	1580760	902078	7045193	3221658	2801812	1026104	1201594	580814
NDW12	15706530	18461566	9469150	18831667	35240057	1201909	8998046	2014573	6092306	2647611	3452120	1.5E+07	1928389	767909	862317	288131	261166	4449094	5500959	2764883	21639219	9837480	9406657	3237626	3453926	1789110
NDW13	13437123	20220502	14482194	11077125	22509613	1566968	8269220	1328668	1420587	631670	1024815	2999292	743941	668590	1111855	548900	265815	1694058	1859770	1269374	8168405	3980184	3384169	1428692	1807108	837073
NDW14	27090204	36555525	21781769	29692719	43494572	2251142	10337211	2515394	5035022	2433920	3261744	9980819	2105526	806483	714843	205672	178947	4756470	5516265	3733538	22716317	10756504	8932554	3618553	4540336	2087618
NDW15	47780144	65304430	37522240	48833045	80208120	4176232	23409311	3353252	7281458	3455135	4293480	1.4E+07	2224124	407647	113055	n.d	n.d	5143240	6580209	4303401	25094196	12554022	10513422	3899548	4915874	2212924
NDC16	58199170	73495149	43422161	62033310	93226295	4361572	33696270	4246386	8081560	4593937	5390882	1.9E+07	2626139	392293	58129	n.d	n.d	5942070	7419183	4444879	24751350	11751577	10197601	3773299	4508606	2146201
NDC17	6318926	6894415	2526535	9756986	15364849	403658	4039057	842835	8862216	3754167	6214397	2.3E+07	2527026	1131277	1359096	378243	338880	5454865	8211305	4351878	24117758	11405451	10865644	4099283	4027585	1982700
TRO01	16331862	16773055	8924003	17856623	27222333	988266	4482461	1799415	19286974	9057558	10837311	3.3E+07	5323501	3813546	6180716	2234740	1891265	13407331	14539191	8939213	62204472	24537387	21102012	7934451	8255503	4619201
NSA02	3772342	4084616	4128941	4186593	7899191	1068506	2393401	1369585	4254193	n.d	8289965	1.5E+07	2804762	9695902	11703401	8700417	4004601	9073283	8180382	5363806	43933220	16793883	9807205	3675047	9203088	3325375
NSA03	1194849	1574412	893822	1292938	2288182	95476	390149	142806	7898465	n.d	10207597	1.5E+07	2899119	384756	637549	258973	257679	3284217	4934697	3184700	23030165	10660801	7594776	3088636	5108917	2501546
NSA04	18751206	23515692	15697915	15487517	25947947	1573376	5531111	1449769	15033399	3191338	4753363	1.5E+07	3440329	4600715	6006194	2980678	1679321	6706402	6115675	3789572	32113962	14625292	9994320	4117038	6625560	3583144
NSV05	3870525	4924896	6091230	4771142	8897653	432910	2353361	719628	12144933	n.d	6871401	9688334	2075470	660781	1144373	478945	369403	2863159	2840983	1162083	13919190	6460078	5262794	1835942	3069446	1463369

IIIb: GC-MS Peak Areas (MAS/TAS HCs)

GC-MS Peak Area (MAS/TAS)																				
Sample ID	MAS-21	MAS-22	MAS-27bS	DiaMAS-27S	MAS-27bR+	MAS-28bS+	MAS-28bR+	MAS-29aS	MAS-29bR+	MAS-29aR	#253	TAS-20	TAS-21	TAS-26S	TAS-26R+	TAS-28S	TAS-27R	TAS-28R	TAS-29	#231
BMD01	335556	359639	345008	n.d	n.d	1353572	3117114	953131	2249248	889541	90	204339	102739	46024	192785	422711	141349	361352	n.d	500
BMD02	110205	75153	109026	n.d	102837	277287	718938	120069	386960	254282	22	85207	68664	15124	192934	308504	113823	286252	11590	570
BMD03	150501	118523	26882	60115	115599	176214	181939	39001	77413	20100	7.8	612429	374800	56997	107439	82172	21395	62267	13755	620
BMD04	371283	291074	328711	n.d	n.d	275150	2187554	155760	558533	97325	28	419572	521431	136918	641261	332024	567166	406191	152416	580
BMD05	164229	119968	145994	n.d	n.d	95658	1206161	194928	437505	319312	660	25102	32381	23006	70144	97206	73055	115652	16231	890
CAN06	163135	209374	19222	107171	32684	420568	946576	244927	502938	193553	15.6	38254	39479	96337	346317	502899	218799	367018	33311	420
CAN07	18644	7030	10338	n.d	5077	25920	54114	14727	25638	12383	2.08	421.94	466.71	605.04	2577	2167	1359	973.42	n.d	630
CAN08	196020	312526	397451	n.d	85472	1070285	2079743	561533	1030011	462589	26.8	53429	61555	203494	979227	1048994	535536	733755	87698	570
KTM01	10245	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.9	n.d	n.d	n.d	8555	12017	n.d	9029	n.d	600
KTM02	8361	n.d	n.d	n.d	n.d	18983	54354	16828	35538	8496	2.28	2667	5449	5323	24824	26445	5478	20587	677.55	540
KTM03	88644	39476	n.d	n.d	n.d	26879	74186	11650	28435	n.d	7.8	96552	50402	n.d	21351	15713	n.d	15786	n.d	630
NDE01	479123	192761	274928	197368	411666	1236359	2235588	688599	1069392	413664	25.6	325801	213742	312248	967253	708524	604849	796448	58271	560
NDE02	241967	65927	207001	126351	260334	715700	1408377	422375	644646	259995	15	683020	573629	998620	3033118	2444072	1574909	2146777	145578	660
NDE03	223048	144329	374459	251798	482398	1308489	2987197	775084	1228567	441067	26	748553	519149	1430473	4273628	3625684	2363021	3062839	186066	700
NDE04	219725	57844	245256	131269	278024	850737	1705401	427774	658491	244223	14	676265	551037	1201511	3487963	2488352	1823317	2242378	171565	640
NDE05	81129	48970	24772	64040	88903	250443	562127	151237	290754	101631	6.8	238969	205564	450678	1281294	1419567	710633	1157271	52237	740
NDE06	298966	90113	266972	300379	515983	1574780	2204091	875257	1328696	504587	28	604089	522588	1601763	4762970	3261950	2406599	3146835	284018	640
NDE07	274976	79325	244337	263885	493791	1461340	3251508	819395	1283666	479464	28	477134	345710	1407059	4500874	3236580	2221346	2817008	214556	680
NDE08	111518	40439	192866	n.d	n.d	632794	1028351	354965	530115	235394	740	215387	100087	116226	515105	597120	347887	553264	n.d	800
NDW09	67980	31650	86588	51650	95754	287160	562277	135082	220095	103337	5.2	277593	192323	352266	873933	682854	498045	623171	51113	780
NDW10	116154	46194	95733	119166	176578	481744	851389	244870	391934	179917	9.2	369767	301589	677126	1988368	1385038	1003089	1310691	186357	720
NDW11	204580	93842	235716	184727	319430	873485	1595950	528566	758454	312548	18	283099	222622	276190	787479	615614	467291	636372	49627	340
NDW12	180517	75954	54769	50545	110909	286978	732112	225832	354030	173574	8.4	507927	283704	312510	963845	844706	602675	903830	36354	820
NDW13	444324	185692	430828	296499	576719	1264141	2822950	940842	1399537	557294	32	550255	464553	954417	2674221	1999016	1303328	1793999	96838	640
NDW14	249942	132697	300814	192700	398010	1107487	2429526	690481	995508	422505	22	1160084	1073511	1393153	4179310	2938562	2200033	2748237	189416	660
NDW15	177258	48317	117776	81314	145367	454066	893416	305764	435466	198418	9.6	761430	656228	632745	1934679	1579565	934641	1326544	n.d	820
NDC16	123692	35745	79770	53305	103202	346776	766633	219080	332238	126606	7.2	613064	413183	453743	1247982	1255948	718908	1019543	n.d	680
NDC17	120011	21720	30988	29521	71381	250737	510612	165480	255977	129507	5.2	313245	145104	124576	385295	351599	199900	351703	8356	740
TRO01	199226	80895	113408	57868	128847	370774	685282	184932	308130	103461	9	1172404	844236	257281	993771	571726	766957	728264	69039	610
NSA02	1383130	594384	576645	1471873	2267825	4424443	7108932	618900	2943709	619209	82	2200277	2220939	1116461	4262602	2502220	2935803	2824970	684871	620
NSA03	184699	121891	85270	n.d	n.d	173629	222090	13959	102787	10121	4.8	236872	215648	57067	259766	167883	167302	144310	28312	400
NSA04	138458	66237	79924	n.d	n.d	134241	194036	10189	74190	10828	4.1	4885	8624	11278	37500	25859	13155	13520	3398	350
NSV05	157499	110341	83732	n.d	n.d	175486	282519	26325	128716	20342	5	33969	61995	42890	166427	158419	81577	107815	26171	550

Appendix IV-a: Migration Study Data (Olefins nd Acids)

Olefin Data

Olefinic Hydrocarbons in Migrated Oils and Extracts																																			
		And-1	And-2	1-4a	1-4b	1-4c	1-4d	1-4e	1-4f-ov	1-4g	1-4col	1-4a2	1-4b2	1-4c2	1-4d2	1-4e2	1-4f2	1-4g2ov	1-4col2	63-1a	63-1b	63-1c	63-1d	63-1e-ov	63-1f	63-1g	63-1col	63-1a2	63-1b2	63-1c2	63-1d2	63-1e2	63-1f2	63-1g2	63-1col2
		Amt of Comp (ppb		Amount of Compound (ppb)																Amount of Compound (ppb)																	
Compor	R/Time	Andrew oils b4 mi		Migrated oils (thru 4mm-1mm particles)																Migrated oils (1mm-63um particles)																	
Hop-17(21)-enes				No detectable n-alkenes and oleanenes																no detectable n-alkenes and oleanenes																	
C30	50.66	2	3	5	6	7	12	15	7	26	1181	7	10	14	24	10	11	16	11	3	3	12	0	17	24	25	932	0	0	0	0	0	0	3	1368
C31 22S	51.83	14	17	11	16	17	28	30	15	29	365	18	19	29	31	17	20	29	47	17	13	30	0	32	30	39	441	0	0	0	0	0	9	22	520
C31 22R	51.95	5	7	6	10	10	17	19	9	21	339	10	11	18	21	13	13	20	16	10	6	18	0	22	23	26	410	0	0	0	0	0	3	12	476
C32 22S	52.66	11	15	6	13	13	20	20	12	27	153	15	12	21	25	19	18	23	28	17	11	21	0	25	24	34	185	0	0	0	0	0	9	16	199
C32 22R	52.93	5	11	10	15	16	26	24	15	31	162	15	16	24	21	13	19	24	12	14	10	25	0	23	26	37	213	0	0	0	0	0	6	15	211
C33 22S	53.74	9	11	6	9	13	19	19	10	22	133	11	12	18	22	15	17	23	20	13	11	20	0	20	23	27	161	0	0	0	0	0	8	16	172
C33 22R	54.15	3	8	6	9	12	18	16	11	20	121	10	9	17	17	12	14	18	8	9	6	15	0	17	18	26	153	0	0	0	0	0	4	13	158
C34 22S	54.89	7	8	5	7	9	12	13	8	16	111	7	8	14	13	12	10	16	14	10	7	13	0	18	15	22	144	0	0	0	0	0	6	15	144
C34 22R	55.54	3	5	3	8	7	9	11	6	12	102	7	7	9	8	9	9	16	6	5	4	10	0	13	10	18	128	0	0	0	0	0	2	10	124
C35 22S	56.19	5	8	4	7	8	10	13	7	14	111	7	8	13	12	11	11	14	13	8	7	13	0	14	16	18	140	0	0	0	0	0	6	12	135
C35 22R	57.11	2	4	4	4	6	6	10	6	13	95	6	6	9	9	12	7	11	4	3	4	10	0	8	11	16	130	0	0	0	0	0	2	6	113
Total (ppb)		**65**	**98**	**67**	**103**	**118**	**177**	**190**	**106**	**230**	**2872**	**112**	**119**	**186**	**202**	**144**	**149**	**209**	**179**	**108**	**81**	**188**	**0**	**209**	**219**	**288**	**3037**	**0**	**0**	**0**	**0**	**0**	**54**	**140**	**3621**
Diasterenes (Diacholest-13(17)-enes																																			
10b20S	42.983	70	99	66	87	97	146	167	106	177	3572	122	122	175	198	127	128	195	395	79	69	169	0	180	191	229	2962	32	0	24	22	15	65	118	5183
10a20S	43.212	330	466	320	409	459	672	791	489	828	12702	580	578	822	882	552	598	909	1186	340	305	800	0	820	886	1103	10474	120	0	91	91	66	278	534	17411
10b20R	44.045	35	60	50	55	78	116	136	87	150	3559	96	91	138	155	74	86	141	187	46	33	132	0	144	154	205	2967	26	0	13	19	14	23	69	4875
10a20R	44.222	174	391	303	381	467	674	830	482	872	14319	566	531	808	923	517	556	887	650	249	257	785	0	813	922	1231	11941	47	0	37	32	18	173	415	19346
24Me10	44.517	312	444	296	394	450	628	752	473	802	11089	542	551	786	844	495	568	833	1072	333	302	754	0	788	856	1063	9378	116	0	86	91	59	257	521	15465
24Me10	45.448	102	172	108	155	185	239	294	197	349	8076	215	203	251	361	190	220	311	742	129	114	292	0	336	349	461	6972	34	0	30	33	14	85	200	11556
24Et-10a	45.64	489	852	594	797	922	1268	1564	948	1647	31876	1100	1099	1573	1696	973	1102	1663	2529	633	556	1572	0	1607	1763	2259	27539	161	0	124	120	77	404	917	44323
24Et-10b	46.69	36	85	38	52	99	92	136	71	131	4585	67	85	128	183	109	109	132	634	73	56	96	0	158	136	139	5169	18	0	16	23	10	42	120	7584
24Et-10a	46.892	238	437	310	428	503	668	830	522	890	23247	580	575	823	911	507	558	837	1566	345	311	838	0	865	939	1229	20275	98	0	74	76	51	237	503	32404
Total (ppb)		**1786**	**3006**	**2085**	**2758**	**3260**	**4501**	**5498**	**3376**	**5847**	**113024**	**3867**	**3834**	**5505**	**6151**	**3544**	**3925**	**5908**	**8960**	**2227**	**2002**	**5438**	**0**	**5711**	**6196**	**7920**	**97676**	**651**	**0**	**495**	**507**	**325**	**1564**	**3396**	**158147**
Me-diasterenes (4β-Me-10α-diasterenes)																																			
C2820S	44.843	53	77	62	78	92	117	152	87	164	19261	117	115	161	167	115	110	178	1643	121	74	184	0	167	179	225	16399	29	0	18	14	9	49	108	27001
C2820R	45.852	33	71	64	79	92	118	157	83	163	21020	107	110	158	142	112	103	177	947	96	62	182	0	165	180	234	18268	14	0	11	9	6	30	97	29118
C2920S	46.109	67	103	68	90	107	137	176	96	188	7866	117	138	189	190	109	134	198	750	105	77	182	0	189	211	257	6759	31	0	21	18	12	58	120	11330
C30S/C3	47.194	30	45	51	0	64	74	0	70	97	0	0	0	118	76	53	82	101	1374	109	59	104	0	116	117	387	8434	0	0	0	0	0	32	67	14301
C29R	47.24	25	73	59	129	103	138	268	74	180	21059	163	197	177	85	79	105	204	574	80	68	174	0	165	191	123	9425	35	0	19	17	13	26	96	14876
C30a?	47.392	17	36	31	34	46	63	82	39	84	4439	44	65	89	89	59	59	88	463	48	32	77	0	80	104	185	3320	11	0	8	6	6	16	55	6639
C30 20R	48.256	50	73	70	85	95	110	139	77	132	24101	100	109	146	132	103	104	141	3467	205	119	188	0	153	164	132	21190	51	0	24	23	16	58	100	35374
C30b?	48.429	21	42	33	51	56	72	92	53	92	7579	67	65	95	94	72	64	91	498	47	36	101	0	95	104	0	6727	6	0	5	4	0	21	46	11003
Total (ppb)		**295**	**521**	**439**	**546**	**655**	**828**	**1066**	**579**	**1100**	**105325**	**715**	**799**	**1133**	**974**	**703**	**761**	**1178**	**9715**	**813**	**527**	**1192**	**0**	**1130**	**1251**	**1544**	**90523**	**177**	**0**	**105**	**92**	**62**	**290**	**689**	**149642**

IV-a: Olefin Data Cont'd

Olefinic Hydrocarbons in Migrated Oils and Extracts (Cont'd)

		63a	63b	63c	63d	63e	63f	63g-ov	63col	63a2	63b2	63c2	63d2	63-e2	63f2	63g2-ov	63col2		8.5	1-4c	63-1a	63-1b	63a	63b
Componen	R/Time	Amount of Compound (ppb)																R/Time	Amount of Compound (ppb)					
		Migrated oils (thru <63um particles)																	olefin content of KCF Blackstone Extracts prior to migration					
Hop-17(21)-enes		no detectable n-alkenes and oleanenes																	no detectable n-alkenes and oleanenes					
C30e*	50.63	8	23	14	2	20	18	10	690	6	10	5	8	5	5	7	242	49.44	49827	0	44059	39130	54264	42004
C31 22S	51.82	23	39	26	14	40	31	20	250	20	23	13	23	19	19	21	130	50.63	2617	0	0	0	1779	0
C31 22R	51.94	13	26	16	4	24	20	11	232	11	12	4	13	11	11	13	104	50.75	12452	0	10623	8985	12553	9600
C32 22S	52.67	19	33	20	12	32	24	18	118	15	17	10	17	14	15	17	73	51.47	578	0	0	101	341	0
C32 22R	52.96	20	31	19	7	33	26	15	116	14	17	8	17	14	15	15	64	51.77	3747	0	3484	2540	3890	2724
C33 22S	53.74	17	26	15	9	27	24	16	98	13	15	11	14	12	15	15	60		0	0	0	0	0	0
C33 22R	54.16	12	23	12	5	24	19	14	88	11	11	5	10	9	9	11	50	52.96	2945	0	2750	2182	3241	2229
C34 22S	54.89	10	19	13	6	23	18	13	84	10	11	8	11	9	9	13	48	53.63	548	0	464	248	556	0
C34 22R	55.52	9	16	9	2	16	13	9	69	5	6	2	6	5	6	7	39	54.21	1882	0	2017	1473	2111	1361
C35 22S	56.17	11	17	12	5	16	13	12	80	8	10	6	10	8	9	11	44		0	0	0	0	0	0
C35 22R	57.11	6	13	10	1	14	10	9	73	4	6	2	6	4	5	8	34	55.56	2207	0	2121	1317	2638	1437
Total (ppb)		**148**	**265**	**165**	**67**	**269**	**216**	**146**	**1897**	**117**	**138**	**75**	**136**	**110**	**118**	**138**	**886**		**76802**	**0**	**65518**	**55975**	**81372**	**59354**
Diasterenes																								
10b20S	42.99	136	249	183	75	230	184	124	2331	116	149	76	148	134	127	146	993	41.86	54177	392	53406	18174	57235	15840
10a20S	43.22	631	1119	818	337	1066	833	561	8144	507	659	318	653	605	588	635	3568	42.09	203545	2441	214624	110725	211071	106363
10b20R	43.98	103	204	135	36	185	129	77	2202	77	110	39	96	97	83	95	815	42.86	55314	44135	56030	50765	59314	53221
10a20R	44.23	608	1158	680	157	1026	740	462	9143	422	558	172	546	511	470	519	3729	43.11	245721	230196	254545	228732	251507	243688
24Me10aS	44.52	612	1068	780	308	1013	789	546	7331	485	626	303	623	575	569	597	3257	43.39	149725	993	162904	81398	188349	83855
24Me10aR	45.45	254	501	324	115	440	334	224	5460	193	263	104	213	238	227	232	2262	44.32	103654	27214	97299	43308	138088	61723
24Et-10aS	45.64	1261	2288	1504	511	2095	1570	1032	21347	911	1223	519	1191	1129	1084	1112	8931	44.52	482465	192292	473743	261759	557532	280774
24Et-10bR	46.69	141	228	150	54	162	131	101	5788	115	129	66	132	123	155	112	2300	45.55	120402	70318	135374	118628	153425	135767
24Et-10aR	46.89	709	1312	784	254	1174	830	544	15768	533	649	236	637	604	567	565	6133	45.76	373346	320752	347162	309959	386969	340502
Total (ppb)		**4454**	**8126**	**5357**	**1847**	**7390**	**5541**	**3671**	**77514**	**3359**	**4366**	**1834**	**4239**	**4015**	**3871**	**4015**	**31988**		**1788350**	**888732**	**1795087**	**1223448**	**2003489**	**1321735**
Me-diasterenes																								
C2820S	44.85	176	358	254	99	323	257	146	12051	163	180	81	170	176	164	154	4757	43.73	348149	9389	353689	221689	394131	232633
C2820R	45.86	176	374	209	56	327	228	123	13674	150	164	59	157	162	132	135	4990	44.73	404874	383604	414573	370399	451020	400824
C2920S	46.12	166	296	201	81	283	222	133	5292	139	167	82	159	160	143	146	2195	44.98	119535	1357	119358	79205	134572	84112
C30S+C29R	47.21	0	0	127	71	225	140	110	5800	123	113	57	104	155	107	103	2683		0	0	0	0	0	0
C29R	47.24	273	516	144	33	241	189	90	6679	124	142	51	145	106	106	117	2610	46.10	298905	134057	257070	182504	291675	201168
C30a?	47.39	78	152	62	29	124	88	57	2676	69	80	36	73	73	60	70	1210	46.24	78627	9146	53159	29327	64045	31529
C30 20R	48.26	256	444	277	118	364	279	166	17343	240	226	119	194	219	206	163	7013	47.13	498821	67069	430741	374237	481104	426115
C30b?	48.44	95	189	108	27	159	110	65	5282	76	78	26	79	81	69	73	1969	47.30	167469	115453	142081	123433	155649	136030
Total (ppb)		**1220**	**2328**	**1383**	**514**	**2046**	**1514**	**889**	**68796**	**1086**	**1152**	**512**	**1080**	**1133**	**986**	**962**	**27427**		**1916381**	**720076**	**1770671**	**1380794**	**1972196**	**1512410**

IV-a: Total *n*-acid (Corrected) Data

Data summary: Total n-acids in Migrated Oils (NSA03→KCF) and Extract Samples

Sample	Sample wt (g)	IStd wt (ug)	SStd wt (ug)	Tot-GC Area	Res.GC Area	Non-Res GCa	DCM Blank Are	Tot Bl Acids (ug)	Resolved blank acids (ug)	Blank n-acids (ug)	Total n-acids area	Contaminatio n / Spike	IStd Area	SStd(5b-Cholanic) Area	Tot.Standards	Total Acids (ug/g)	Resolved Acids (ug/g)	n-acids (ug/g)	Response Factor	Corr. Total Acids (ug/g)	Corr.Resolved Acids (ug/g)	Corr.Tot.n-acids (ug/g)
63a2	0.164	9.86	10.00	3768	580	3187.468	2834.468	25	13	1	13	51	257	150	406	-43	-49	0	1.05	-78	-89	0
63a2b	0.156	9.86	10.00	4012	677	3335.002	3189.762	25	13	1	20	20	252	214	465	-78	-33	2	1.05	-97	-41	2
63b2	0.152	9.86	10.00	3660	682	2977.923	3402.941	25	13	1	17	62	227	186	413	-229	-24	2	1.05	-298	-32	2
63c2	0.163	9.86	10.00	3950	721	3229.333	3642.838	25	13	1	13	59	170	193	364	-196	28	1	1.05	-183	26	1
63d2	0.168	9.86	10.00	4541	820	3720.655	3515.455	25	13	1	27	105	202	198	401	0	16	5	1.05	0	17	5
63e2	0.161	9.86	10.00	4292	716	3576.501	3498.666	25	13	1	38	65	174	234	409	-45	6	10	1.05	-36	5	8
63f2	0.155	9.86	9.97	4618	944	3674.259	3427.573	36	18	1	31	111	328	206	535	-125	-59	-1	1.05	-209	-100	-1
63f2b	0.157	9.86	9.97	4762	919	3842.638	3596.612	36	18	1	56	71	291	186	477	-94	-36	5	1.05	-156	-59	9
63g2-ov	0.163	9.86	9.97	4281	840	3441.200	3377.065	36	18	1	36	96	248	154	402	-120	-28	2	1.05	-204	-48	4
63col2	0.155	9.86	9.97	6302	1431	4870.860	3618.796	36	18	1	347	78	193	236	429	488	188	108	1.05	421	162	93
63-1a2	0.163	9.86	9.97	4261	743	3518.098	3885.391	36	18	1	32	98	160	211	371	-254	-8	6	1.05	-204	-6	5
63-1b2	0.166	9.86	9.97	4452	696	3756.016	4027.011	36	18	1	39	99	172	242	415	-245	-47	7	1.05	-185	-35	6
63-1c2	0.167	9.86	9.94	4117	634	3482.420	3096.690	-1	9	1	44	92	123	176	299	307	61	13	1.05	226	45	9
63-1d2	0.154	9.86	9.94	3853	760	3093.010	3321.830	-1	9	1	47	48	192	239	431	24	34	7	1.05	20	29	6
63-1e2	0.156	9.86	9.94	3631	557	3073.540	2660.750	-1	9	1	13	85	231	166	398	140	-39	-5	1.05	205	-57	-8
63-1f2	0.151	9.86	9.82	3296	641	2654.800	2326.760	-1	9	1	25	92	210	165	374	163	-7	-1	1.05	216	-9	-2
63-1f2b	0.157	9.86	9.82	3698	951	2747.190	2397.640	-1	9	1	40	181	256	253	508	156	5	1	1.05	165	6	1
63-1g2ov	0.166	9.86	9.94	3976	963	3012.870	3076.490	-1	9	1	66	147	287	252	539	50	2	5	1.05	60	2	6
63-1col2	0.163	9.86	9.92	6241	2026	4214.830	2571.110	40	19	1	692	47	215	227	442	648	317	190	1.05	646	315	190
1-4a2	0.165	9.86	9.92	3972	794	3177.660	3388.580	40	19	1	28	84	248	229	477	-238	-58	2	1.05	-271	-66	3
1-4b2	0.157	9.86	9.92	4713	1168	3545.170	3178.060	40	19	1	83	63	326	286	612	-90	-25	11	1.05	-108	-30	14
1-4c2	0.162	9.86	9.92	3891	704	3186.920	2966.340	40	19	1	19	73	185	178	364	-88	-29	2	1.05	-96	-31	2
1-4d2	0.165	9.86	9.92	3839	857	2982.480	2536.900	40	19	1	49	93	285	175	460	-87	-51	6	1.05	-148	-87	10
1-4d2b	0.167	9.86	9.92	3962	834	3128.010	2836.080	40	19	1	56	57	271	172	443	-104	-40	8	1.05	-172	-66	13
1-4e2	0.164	9.86	9.89	3767	772	2994.370	3143.620	41	18	3	24	87	215	211	425	-220	-34	-9	1.05	-235	-37	-10
1-4f2	0.158	9.86	9.89	4072	784	3287.940	3413.480	41	18	3	35	42	204	229	433	-203	-16	-6	1.05	-190	-15	-6
1-4g2ov	0.164	9.86	9.89	4018	804	3214.200	3036.700	41	18	3	43	90	194	248	443	-111	-23	-3	1.05	-91	-19	-2
1-4col2	0.154	9.86	9.89	7386	2436	4949.620	3339.400	41	18	3	617	148	439	482	920	169	86	73	1.05	161	82	70
1-4col2b	0.172	9.86	9.89	4600	1076	3523.450	3267.050	41	18	3	273	124	201	160	361	3	66	63	1.05	4	88	83
And1	0.158	9.86	9.89	4315	688	3627.200	3234.940	41	18	3	43	87	176	156	332	-26	-16	-1	1.05	-30	-19	-2
And2	0.157	9.86	9.89	4688	711	3977.250	3629.790	41	18	3	32	62	167	139	306	-2	17	-5	1.05	-2	22	-6
1-4eom	0.144	9.86	9.86	43281	23243	20038.590	5112.100	10	9	4	6567	241	133	176	309	19342	11649	3358	1.05	15243		2647
63-1eom	0.147	9.86	9.86	29232	10776	18455.920	4742.130	10	9	4	1589	165	107	61	168	15045	6474	964	1.05	27551	11856	1766
63eom	0.121	9.86	9.86	26249	4472	21777.420	5174.210	10	9	4	1616	207	98	22	119	17182	3376	1309	1.05	80819	15881	6157

Migrated Oils (particle sizes):			Column Extracts	Initial oil
<63µm	63µm-1mm	1mm-4mm	Important data columns	Rock Extracts

IV-a: *n*-Acid Data (Estimated)

Estimated values for individual normal and isoprenoid acids (ppb)																										
Sample Gp	Sample	n-C12	n-C13	n-C14	n-C15	n-C16	n-C17	n-C18	n-C19	n-C20	n-C21	n-C22	n-C23	n-C24	n-C25	n-C26	n-C27	n-C28	n-C29	n-C30	n-C31	n-C32	n-C33	n-C34	Pr-acid	Ph-acid
NS oil	NS-1	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.
	NS-2	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.	neg.
	Migrated oils																									
4mm-1mm	1-4a2	0	0	0	1099	3310	307	2869	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	301	660
	1-4b2	297	0	477	2199	8108	1103	5716	0	265	484	292	0	256	0	0	0	0	0	0	0	0	0	0	838	1041
	1-4c2	0	0	0	1328	599	384	4370	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	997
	1-4d2b	0	0	568	2104	8873	1038	6729	434	416	0	0	0	0	0	0	0	0	0	0	0	0	0	0	644	904
	1-4e2	0	0	829	1408	697	507	3648	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	378	1000
	1-4f2	0	0	748	1339	3969	799	3072	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	483	571
	1-4g2ov	0	0	673	1335	4940	602	3389	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	393	830
1mm-63um	63-1a2	0	0	731	1454	4249	313	2971	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	319	464
	63-1b2	295	0	754	1397	4894	0	2859	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	277	664
	63-1c2	0	0	1305	1938	6832	753	4813	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	636	1057
	63-1d2	314	0	875	1739	6173	518	3745	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	601	708
	63-1e2	0	0	455	1275	2522	0	1014	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	511	0
	63-1f2b	218	285	1114	2030	4693	642	1437	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	707	746
	63-1g2ov	340	268	1272	1831	7023	788	4469	0	301	0	0	0	0	0	0	0	0	0	0	0	0	0	0	760	1019
<63um	63a2b	0	0	783	1428	2687	0	1315	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	63b2	0	0	1126	1290	2074	550	1442	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	63c2	0	0	428	1234	2021	0	720	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	338
	63d2	0	0	477	2158	3931	0	1810	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	690	430
	63e2	0	0	603	1327	6741	0	1794	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	280	380
	63f2b	343	497	1584	2799	8991	933	4755	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1012	1144
	63g2-ov	0	0	1014	2135	7149	615	3926	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	573	748
Col. extract	1-4col2b	447	2423	5867	7445	15825	6870	11603	4090	3782	2648	4977	2862	8778	1521	3664	988	2671	1104	1991	901	1078	9792	1217	3099	3016
	63-1col2	3512	6541	12245	12948	27760	14700	22149	8618	8697	5437	11197	5252	19879	3044	9175	1833	5869	2038	4403	1051	2399	779	3257	8646	6191
	63col2	2929	5611	8356	8014	17218	6743	10924	3737	3629	2295	4528	2261	7656	1257	4220	848	2215	907	1715	395	879	0	1729	3421	3208
Rock extract	4mm-1mm	146588	156471	182280	156296	269664	189255	211672	123410	122824	106418	150045	89405	178067	59037	58870	45530	59204	50838	53193	37819	37661	31345	51639	47897	59797
	1mm-63um	161370	147403	102302	99391	105820	140871	103597	70848	59504	86867	41950	21794	75099	67262	50588	31729	75386	68579	73816	13063	69026	19342	1157	154610	75913
	<63a eom	319670	323274	244856	259147	555267	385971	327158	170787	338218	378018	188434	228855	304695	104423	125094	240040	237523	201110	274123	31224	235007	89137	100011	399642	186694

IV-a: Hopanoic Acid Data

C30-C33-17,21(H)-Hopanoic Acids (ppm)																														
			63a2	63b2	63c2	63d2	63e2	63f2	63g2-ov	63col2	63-1a2	63-1b2	63-1c2	63-1d2	63-1e2	63-1f2	63-1g2ov	63-1col2	1-4a2	1-4b2	1-4c2	1-4d2	1-4e2	1-4f2	1-4g2ov	1-4col2	And1	And2	4-1mm	63um-1mm	63um
C-number	Isomers	Ret.Time	Mig. Oils							Col.extr	Mig. Oils							Col.extr	Mig. Oils								N.Sea oil		Rock extracts		
C30	ab22S	54.247	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.03**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.03**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.01**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ab22R	54.297	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.03**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.03**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.02**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ba22S	54.648	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.05**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.03**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ba22R	55.067	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.05**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.02**	n.d	n.d	**0.00**	**0.00**	**0.00**
	bb22S	56.091	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.06**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.09**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	**0.00**	**0.00**	**0.00**
	bb22R	56.57	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.06**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.13**	n.d	n.d	**1.73**	**0.00**	**0.00**
C31	ab22S	55.905	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ab22R	56.302	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.12**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.12**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.06**	n.d	n.d	**3.50**	**0.00**	**0.00**
	ba22S	56.695	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ba22R	56.938	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.10**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.11**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	**2.38**	**0.00**	**0.00**
	bb22S		n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	**0.00**	**0.00**	**0.00**
	bb22R	59.069	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.53**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.85**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.27**	n.d	n.d	**26.12**	**11.83**	**6.54**
C32	ab22S	57.737	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.05**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ab22R	58.282	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.60**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**1.08**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.30**	n.d	n.d	**24.85**	**0.00**	**0.00**
	ba22S	58.686	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.02**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.10**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.01**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ba22R	59.037	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.33**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.65**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.18**	n.d	n.d	**18.08**	**0.00**	**0.00**
	bb22S		n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	**3.43**	**0.00**	**0.00**
	bb22R	61.8	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**2.84**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**5.58**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**1.44**	n.d	n.d	**181.77**	**61.46**	**47.99**
C33	ab22S	60.168	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.08**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.19**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	**4.78**	**0.00**	**0.00**
	ab22R	61.101	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.10**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.23**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.05**	n.d	n.d	**5.70**	**0.00**	**0.00**
	ba22S	61.206	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.16**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.13**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.04**	n.d	n.d	**0.00**	**0.00**	**0.00**
	ba22R	62.314	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.13**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.31**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.07**	n.d	n.d	**5.20**	**0.00**	**0.00**
	bb22S		n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.00**	n.d	n.d	**0.00**	**0.00**	**0.00**
	bb22R	64.552	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.65**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**1.52**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	**0.34**	n.d	n.d	**49.14**	**13.21**	**11.65**
Total, ppm										**5.99**								**11.28**								**3.10**			**326.68**	**86.50**	**66.19**

Appendix IV-b: Migration Study Data (Biomarkers, PCA Data Set)

n-alkane (GC Peak Areas)

		n-alkanes (GC peak areas)																												
		nC10	nC11	nC12	nC13	nC14	nC15	nC16	nC17	Pr	nC18	Ph	nC19	nC20	nC21	nC22	nC23	nC24	nC25	nC26	nC27	nC28	nC29	nC30	nC31	nC32	nC33	nC34	nC35	nC36	Int.Std
Part. size	Rep1- Migrated oil & col. extract																													
4mm-1mm	1-4a	18329	283878	686557	836039	11-May	889863	787690	673791	393222	602996	304250	509340	502863	411017	380837	331799	309931	264319	244264	162086	128901	78959	61949	38500	21131	6701	31979	n.d	n.d	449303
	1-4b	74165	371366	763665	898908	882065	929721	832918	729641	407342	650045	323715	546924	522758	429859	409738	356340	333068	285486	261098	180056	145330	92829	69928	40613	23726	17828	33012	n.d	n.d	597765
	1-4c	76903	390472	862962	1002588	995361	1056065	949032	825265	451366	735703	367104	619464	609832	498464	475071	420752	395126	332504	315816	208475	166732	107045	78851	51284	26528	11371	21908	n.d	n.d	650324
	1-4d	19117	256199	702878	921005	930144	994968	885704	778692	427575	693623	345378	590295	572192	465262	443512	394888	364504	309129	296501	195850	153595	100848	76000	53112	25451	9196	21004	8066	8559	664384
	1-4e	155931	565043	970713	1042054	988460	1039076	931282	809154	442292	720003	357873	615219	582412	490219	456719	417366	386853	332211	287498	208416	164064	107838	79828	47494	26673	9878	42135	8130	5473	566386
	1-4f-ov	150845	661361	1104841	1212633	1190427	1255680	1133471	991294	530700	865799	407963	756279	743069	616473	564474	514580	480462	410615	383181	261605	204015	135355	99299	58714	35057	10888	38360	11363	12475	675976
	1-4g	161509	641229	1014188	1064918	1025637	1074412	959762	844731	462245	755561	376987	637581	623901	504534	483076	432877	402597	341125	320292	217518	172263	113091	86957	58439	28733	11799	7966	8715	11312	638091
	1-4col	173819	738768	1160210	1318717	1263727	1335832	1188870	1047571	571212	945677	484364	790050	768322	623901	581715	514632	483247	413203	367421	261659	208348	133719	101284	59250	35981	20435	42266	12132	12150	640704
1mm-63um	63-1a	19820	115972	685569	1096318	1197494	1313567	1186089	1053113	577466	954042	495526	800128	780261	636988	587481	515162	478107	410144	362994	275352	228509	159564	123182	85925	45166	34136	46112	10064	11137	752242
	63-1b	30067	145018	701656	1041805	1092841	1172250	1043432	880049	452681	795481	370992	697110	667121	564753	523205	466931	431578	363084	334217	222189	172401	107646	80309	56057	27760	19516	47610	9859	n.d	671919
	63-1c	110283	522315	928695	1066241	1052825	1111090	996713	869181	470583	757303	361915	660470	651596	537405	502894	445569	414147	348200	322902	207728	156167	94182	62601	45294	22809	4337	32873	8031	8745	698844
	63-1d	14711	271469	746755	976252	995983	1023990	972486	855238	463165	771968	376711	659631	649333	535841	499607	442676	409199	351962	310237	211231	162996	98158	71899	41866	23658	17734	27314	11246	n.d	583055
	63-1e-ov	146397	630821	1015880	1140267	1093944	1152708	1017921	887428	486708	787318	391343	658074	620174	515308	491452	437918	403133	342332	317842	213110	164780	103256	77977	54272	25068	19934	36267	8910	2831	552420
	63-1f	83639	450344	888972	1032367	1020741	1080053	971333	836750	451262	752232	367423	643375	607605	507494	480517	433334	404524	346347	325727	225865	179923	120459	92205	62381	32339	22344	32660	8737	9864	583811
	63-1g	120899	529486	895246	1004993	991448	1055049	950477	828085	449732	739286	364954	634815	607900	500656	470978	425447	391355	330133	310510	210701	170032	114784	87777	55231	32604	24687	38141	8271	11256	646357
	63-1col	88241	486138	974740	1149775	1133625	1193545	1067702	927078	502178	818737	400000	701695	681974	569741	532864	490436	471241	426270	416253	309385	254459	182751	134630	92807	51919	31009	60228	11611	14940	584659
<63um	63a	17676	192745	686537	931142	951622	1018067	922344	806682	439282	708381	337690	618410	591431	500946	474225	422695	392560	333377	305025	202361	160273	103488	74061	48219	25004	9902	39084	8339	n.d	520946
	63b	161720	692930	1146014	1258401	1241483	1315843	1183322	1032177	559057	923285	449624	787002	766421	627040	582078	522714	489274	426323	410802	297215	244748	169757	120899	77034	44485	31446	59172	11680	10369	725584
	63c	171790	669654	1096575	1226492	1180343	1250229	1134205	994947	535662	880561	422851	763544	746613	619757	588533	523314	476754	392326	336913	214884	160721	88450	65550	35215	22053	16232	46607	10116	9071	565793
	63d	65804	527268	1347268	1687652	1.69E+06	1833731	1651261	1471658	795417	1344110	706178	1113913	1105360	893547	833882	733722	665916	548165	495578	310821	234874	133842	94870	62057	28267	25926	63629	16209	16480	1080356
	63e	20923	139817	665101	1019392	1071566	1160834	1053315	925111	502793	799934	374061	697565	693253	571534	537951	480922	449142	388158	344904	261467	214743	149672	114052	73343	40566	30644	57217	9019	11664	619354
	63f	17304	121216	581288	898317	940240	1020492	922916	803860	436686	703056	328186	617664	602723	500568	464626	407006	381653	331086	310191	209795	167705	111319	76545	50074	27137	18562	21545	9351	9696	539113
	63g-ov	20033	27813	380088	799428	929901	1036183	947240	831776	448137	736762	356659	631387	618165	510021	480128	416332	395845	338099	312021	215160	170627	110977	82982	53107	28819	22587	41444	8204	10979	526544
	63col	16787	241023	754525	1010644	1030389	1107099	998003	875692	474626	768945	366933	661913	633629	526954	505681	458155	425162	371359	352300	248055	201103	135575	99820	68265	37517	26961	24710	n.d	n.d	577889
	Rep2- Migrated oil & col. extract																													
4mm-1mm	1-4a2	60527	303556	663137	804549	811761	871223	788113	704883	373312	634047	305903	544815	536761	450238	431951	379855	355927	306564	274850	191550	152186	99683	73396	48854	25309	9977	34845	9721	8088	571010
	1-4b2	14614	264643	735259	950622	955831	1018942	917526	802717	430162	721048	347239	610468	604176	496489	476963	426451	395688	336836	320227	214222	168585	109138	81912	54040	27750	10985	36435	9138	9310	596805
	1-4c2	67638	428158	946127	1131273	1125537	1184741	1046767	919301	497156	814967	401608	694318	674685	550996	520601	460670	433686	372077	344937	236041	187130	121082	88413	59235	30286	11702	40332	9181	n.d	628742
	1-4d2	56017	366593	884702	1071834	1073979	1137852	1019150	877340	473223	789515	391487	677097	646408	549560	510133	458600	418871	360044	301721	228711	181046	118689	85265	56591	29954	9322	41646	9096	8875	576707
	1-4e2	16503	326272	944522	1195454	1185416	1251097	1102412	966384	524072	856188	422925	722437	711314	594842	552601	482645	455097	384911	361854	247545	196930	125450	93853	54497	31378	6143	51192	9071	10347	608357
	1-4f2	16270	221469	747125	1064136	1101333	1180281	1053872	922941	501143	812504	401057	711102	696868	574928	536668	477471	440725	368310	350279	241130	189644	123529	89503	54027	30792	22371	41082	9053	2762	597836
	1-4g2ov	72227	449875	963646	1147177	1130474	1193460	1055866	939933	512271	839811	407742	712466	700397	577232	537808	479173	436618	373972	345890	235239	187958	122891	90898	53561	32036	24684	40630	8985	10617	614603
	1-4col2	85750	580910	1259442	1493610	1458569	1539444	1363272	1203203	651137	1071518	525005	898693	851623	732911	679937	607183	560566	479158	445090	303816	245924	166260	120302	77746	49570	30300	50464	11974	14068	653720
1mm-63um	63-1a2	123045	614791	1066521	1206200	1164401	1233896	1100684	956643	513626	866653	421516	743030	734925	611667	566832	508545	474490	409234	391226	280954	235758	166825	125852	84320	53082	34439	47422	12349	3420	611769
	63-1b2	17707	155906	713599	1055744	1127996	1216842	1099159	968019	525215	854095	411300	737656	727815	582922	558614	498054	468013	409931	392112	308536	270259	204221	156246	101383	65733	43175	61757	8742	15007	651049
	63-1c2	77185	369276	723148	861160	850515	902517	810885	707472	384215	616640	285879	541572	525404	428100	409526	363268	340385	297067	288400	210240	179538	130084	97865	65228	36882	20925	34255	6847	9242	633800
	63-1d2	15729	118335	523358	787519	832613	885268	783732	711618	384521	629761	293753	542752	533001	435069	406248	367598	341546	295318	278390	183202	142134	90462	66175	39047	23431	9521	35388	6577	10314	624983
	63-1e2	16982	132483	610822	939839	990244	1080413	982321	846781	453673	755208	361626	660096	645750	520883	496079	441988	412348	355817	331692	251985	216486	158455	125002	82474	48413	32054	45429	8447	11848	668191
	63-1f2	79030	448413	940812	1071911	1061906	1121953	1006434	877204	476225	783582	381048	675841	662111	547097	508659	457712	421165	365580	350714	244246	207201	145024	112572	73932	41486	19270	44389	10646	12371	639970
	63-1g2o	72154	470242	1061113	1293824	1295606	1329019	1259299	1099268	591574	959984	457063	827649	807165	665878	620397	546841	509366	436435	404046	277765	219721	146060	101321	70831	37974	12098	44652	10614	10385	706103
	63-1col2	77999	442349	940387	1142593	1127725	1195089	1062020	927082	505092	826758	405419	700108	695228	567865	538834	489405	463281	412144	394534	288810	235304	165344	120736	81410	42908	29481	44842	8200	13187	570275
<63um	63a2	20953	86168	610039	1044811	1141565	1233241	1121138	985603	531505	879859	427385	759843	725196	608438	578553	515735	476330	407923	343275	237481	179348	107137	79704	46860	25268	6405	43949	11336	10726	614650
	63b2	65438	446685	1035978	1279442	1254632	1321229	1189598	1028167	553168	933483	453857	796962	763568	620638	577415	525719	491335	417333	379152	251576	196328	120524	89926	60298	24093	25709	47653	9286	10714	727644
	63c2	15545	101551	654905	1062208	1135885	1233038	1104395	969420	524018	848872	387007	741958	727417	598862	557725	485896	455850	388586	340038	232779	176767	104701	78024	49328	25619	7320	27876	10378	8780	642044
	63d2	40709	298356	783424	990976	999724	1071281	966687	845029	457421	741828	346737	647699	639460	521230	492153	429225	403175	340135	286183	199843	148890	88946	63687	38950	19436	5000	34483	9593	10324	622419
	63-e2	16962	89981	580401	946763	1005280	1044161	992293	865022	470202	761037	363097	664012	645926	546070	507676	450002	413074	353214	316845	209417	157914	93917	69341	41444	20824	18263	34537	8275	11029	583469
	63f2	14470	50384	452559	837077	927339	1025281	935845	809810	435392	731852	362719	631758	606416	506888	476267	428196	393340	335485	308935	202405	153187	91227	66586	41246	22073	17283	18791	10425	7843	554485
	63g2ov	17550	129756	626143	1013713	1071199	1160328	1039485	894822	483501	813000	403530	695914	680106	561566	522097	456298	430300	377501	351482	240044	191990	124491	92863	63940	30685	22797	22741	10487	10701	658323
	63col2	15228	180130	761574	1092412	1119140	1193167	1058003	928974	504860	823095	401704	706071	685477	580431	537313	478377	444393	379280	329709	244854	195700	126732	94928	63312	32300	6152	26428	9208	15214	578239
Initial oil	NS-1	16400	187870	700391	976940	990896	1017375	967999	853485	465268	762951	378450	646554	616972	521545	480314	434724	401909	345303	330541	219605	173535	117882	87002	57200	30778	22007	40192	8557	n.d	654798
	NS-2	23935	94489	569832	937294	1032320	1124762	1020331	891959	482151	775800	387823	692224	682441	564501	527164	468672	435280	369075	339448	233806	183846	123207	88180	52644	31804	10675	38127	8619	3099	631164

IV-b: Steranes (GC-MS Peak Areas)

		GC peak area (Steranes and Diasteranes)																				m/z 218-abb-St (p.a.)								m/z 259 ba-diasteranes (p.a.)							
		C27-20S	C27-20R	C28-S'a'	C28-S'b'	C28-R'a'	C28R(a+b)	C27aaS	C27bbR	C29-20S?	C27bbS	C27aaR	C29-20R?	C28aaS	C28bbR	C28bbS	C28aaR	C29aaS	C29bbR	C29bbS	C29aaR	C27bbR	C27bbS	C28bbR	C28bbS	C29bbR	C29bbS	217 max pk	Int. Std	St27dbS	St27dbR	St28dbS(1)	St28dbS(	St28dbR(	St28dbR(	St29dbS	St29dbR
Particle size	Sample	Rep1- Migrated oil & col. Extract																																			
4mm-1mm	1-4a	110560	66206	47889	62995	28631	36830	37556	110144	107497	52815	32827	90442	37037	37301	54537	30466	32485	55323	37279	32904	72131	49553	41931	50542	62286	47938	2534962	8806281	72756	50281	43321	40445	23950	15731	57153	45432
	1-4b	88772	56448	37911	49544	13981	19676	27819	86259	83597	39439	24578	69796	31989	29630	43802	26879	24499	32532	29205	23792	58169	44405	36952	43084	36623	35914	2490231	8583869	58811	40329	29401	30354	24410	18720	44878	36343
	1-4c	138093	87267	72412	70029	33582	30664	45534	136529	132249	63869	39159	111856	50970	46386	70440	37937	40334	67369	45833	35400	99853	63652	61862	71807	59326	67158	3521363	12083815	84854	64843	43165	49341	47702	28335	73215	54097
	1-4d	135428	88701	71951	67331	30664	42593	45385	143934	130026	62874	39828	109388	48481	45821	67661	35553	39544	65808	43913	41128	96310	67319	61174	69619	59041	66178	3591800	12392015	88732	62672	55502	45251	46839	18249	69209	53050
	1-4e	138001	83818	53415	74943	36052	29019	46177	138994	135585	92168	40360	113111	49642	47912	69154	36904	41461	70199	45574	35154	94056	69671	62319	71491	61416	66360	3149815	10969327	89311	60158	43920	49129	29184	28976	75059	54183
	1-4f-ov	104165	74005	56042	53034	26601	34372	36943	107492	102576	61962	33318	89336	57838	36607	55189	27492	32696	39960	35558	30889	73721	56629	50188	57482	49880	53008	2560114	8829131	73080	50849	47673	35925	20741	14238	57205	44168
	1-4g	114478	76991	53322	57762	36950	44797	39616	120449	113466	56226	34499	95676	43356	40865	61066	33176	36422	63459	40907	28953	85773	59358	52995	61303	72712	55538	2832208	9776569	74043	52380	38284	41968	24330	21324	60334	49744
	1-4col	100459	66135	58022	52938	34273	41739	38125	106081	103548	51475	39999	85559	38152	36969	56807	31808	31966	54024	33912	31325	72044	49259	48019	56423	49219	52130	2088579	7193161	66599	42261	33840	34357	21238	20200	53240	41670
1mm-63um	63-1a	95070	59339	53095	48539	31081	26100	31311	96211	90963	47490	29341	77946	36186	33933	49738	31808	51738	33803	38376	34200	64465	52807	43210	49943	59467	43298	2252043	7793957	62299	43262	36561	27683	20320	19323	49445	38993
	63-1b	98962	66037	54223	48114	15961	28916	32191	100218	99697	54612	29983	83292	34361	31818	48674	21423	22489	32633	26573	26970	69017	51449	51774	48426	46162	51637	2422580	8320814	65773	42316	40030	28500	20413	12455	50562	41201
	63-1c	94160	58303	41172	51338	13014	26950	32257	91785	92397	46938	29476	75645	35938	32633	48713	25811	30047	50080	33599	23634	65076	48156	42838	49775	58987	46430	2495210	8591081	61364	43232	30583	30366	31271	16088	51933	38648
	63-1d	84194	57510	34860	45936	25652	22660	30137	88499	84920	42160	26144	72084	35212	31115	45865	24461	25869	46262	28710	22390	60072	45569	39544	46296	40197	42647	1976890	6825292	53541	37892	30426	30621	18129	15749	41127	36424
	63-1e-ov	107218	70935	47461	60514	36030	30928	35059	102575	104792	55230	33849	88206	41433	37333	56365	29135	33208	41859	38630	29795	46.961	47.093	48.355	48.478	49.472	49.585	2225796	7675428	65188	48714	36838	29377	20393	20430	54296	43992
	63-1f	112426	71974	59979	57446	36909	46807	38202	112069	105007	56125	36159	90377	41447	39087	57797	30210	33693	57236	37430	29375	76702	54598	51247	59145	51498	56417	2526552	8680588	70137	50865	47379	38981	36444	14157	58066	46506
	63-1g	92184	58515	39771	49835	28439	24169	26519	87931	87618	47754	27917	73916	33280	30968	47120	24693	27003	33885	31892	25865	60699	46885	40205	47271	40278	44276	2192456	7540425	58859	42093	38423	27931	18084	11285	45308	35683
	63-1col	108924	70246	41939	59379	24668	35780	35470	110612	103524	50191	37011	85420	35852	35064	51419	23858	24407	44689	27653	28422	71489	51726	47001	53179	45344	50275	2288034	7780675	66963	47139	28026	32354	31323	18259	57313	43545
<63um	63a	121754	77819	52069	65087	29144	30319	36702	119463	112054	54942	35649	90447	40606	39096	56823	30673	42023	53956	37018	27067	76200	61110	51001	57874	46906	53721	2659657	9151848	76414	50580	48811	41140	32825	19913	63598	47262
	63b	108186	71794	58629	57090	22980	34497	29754	100702	101835	51575	31373	86427	36046	35879	52634	27864	27293	49886	35226	29236	68250	48932	46361	53644	43036	52518	2466750	8542216	69133	47786	42531	36711	29868	18522	52502	42609
	63c	106260	72717	46049	58987	44064	32121	35407	103486	101508	51433	30096	87115	36419	34449	52780	26795	30746	48091	33595	23589	69484	49698	45527	53147	43362	50099	1961580	6718936	63753	48118	44620	37277	34957	20248	57202	41419
	63d	87782	54791	43272	40484	20313	27344	29253	89188	83317	42299	26040	70833	32293	29817	44869	24214	23243	40449	28843	21491	58686	39598	37825	44839	47624	36800	2063940	7076738	57682	39116	26245	28974	25450	14354	44692	35355
	63e	99203	60641	52619	50948	21916	31460	29177	103168	95399	47929	28858	80942	35766	33439	49530	27809	28056	34600	34039	28544	65144	48306	43005	50290	39791	46019	2104716	7181458	62721	43055	37244	29637	27615	18001	50567	39254
	63f	99389	62807	52769	52301	40728	30421	33958	101362	98244	52215	30773	80088	35967	34371	49871	26812	27873	47075	32637	28675	68058	50430	44889	52121	40818	45876	2157321	7378396	65115	46436	29734	35752	31424	19134	56202	41044
	63gov	114980	70490	43152	63892	43130	33758	35602	116177	110300	53262	32960	93173	35437	36903	56322	26921	31786	52115	37943	23469	79185	52570	49751	59066	45045	54465	2349921	8003767	72249	50289	44534	39813	31363	20378	56974	45618
	63col	129159	87027	56410	73169	45282	37342	43955	133653	123694	64409	52210	101564	43729	43923	65548	36185	42599	51010	37658	36685	87039	69304	57679	65022	68847	61374	2856313	9552335	82484	57474	44141	40692	37388	23920	66231	51651
		Rep2- Migrated oil & col. extract																																			
4mm-1mm	1-4a2	99336	64505	42568	54133	28447	37362	32309	96456	91664	52633	28626	76079	32960	31336	47463	25355	28841	49604	32356	33265	61169	48240	40425	47454	53955	43143	10224316	3045373	63739	36549	36406	31557	19486	14885	51774	35305
	1-4b2	96337	61131	41303	53284	21481	20252	32282	93310	87397	42884	26084	77321	30473	29700	45818	20129	20898	30299	26150	24965	63770	47488	42434	49045	56764	46555	7916351	2320357	58881	41443	29174	33984	20134	19730	48384	37116
	1-4c2	105564	66088	55744	55774	32654	43763	39826	113651	105246	53873	31428	89073	39244	36332	53307	29296	28577	52989	36413	26333	71228	57739	47515	54675	45453	51292	7736972	2261369	70754	48665	40227	36844	23696	24738	54492	41275
	1-4d2	87627	59987	47181	45992	30274	35387	30365	88290	83427	42870	25287	71607	32348	30052	45061	23060	24777	44431	30592	20078	57987	45684	39020	45238	38708	42645	6337269	1864565	57258	39706	38206	30268	19406	18367	43467	35278
	1-4e2	98966	59388	36869	52328	25037	24238	31353	100609	95298	45732	28070	80862	32789	32861	48544	25307	27398	45475	32093	26831	63338	49484	42874	49387	40387	47944	6785763	2001755	62042	41594	26829	29660	15914	18408	53482	38322
	1-4f2	115066	75793	58398	59735	27032	39344	37725	105832	106956	51229	31469	90611	37957	38212	55879	31300	31813	51872	39852	24635	72018	55101	49369	55910	62498	54224	7679101	2230206	74531	50191	33557	39070	20062	22651	59998	43973
	1-4g2ov	80241	48218	37554	36376	22754	31093	28340	84204	70628	38019	26001	64056	37544	27915	42022	22975	23723	31235	31013	20467	52790	41018	36488	42099	36046	42645	5673891	1640118	51612	34075	23675	25532	25212	10476	37441	34476
	1-4col2	93705	57996	47467	49388	38453	28636	32511	94791	91968	63048	29871	76465	35645	32770	47822	26458	27089	46379	31560	23899	62607	44685	42334	48098	40729	47414	5613430	1641028	57551	40368	35968	33709	19502	19421	49630	37786
1mm-63um	63-1a2	108288	68540	55333	58891	23336	25193	37404	102771	109136	54524	33356	89037	40236	37594	54649	28911	37273	46921	34076	25996	71007	55974	49079	55978	55535	48935	7020371	2067615	68256	45929	37422	33237	17319	21526	52182	44491
	63-1b2	103450	65914	53593	55361	23889	23302	34634	106315	96371	51069	32728	84644	38034	35966	54212	29073	27494	61645	29724	30028	72883	49129	47454	55473	53516	48133	7155306	2093006	66428	47176	37822	33253	31463	19742	56682	40728
	63-1c2	80711	50529	30969	44539	33390	24746	26674	81828	82350	55327	23242	66917	29579	28029	42017	22750	23681	41635	28087	25509	54740	41379	36581	42523	34408	40050	7825714	2294942	52139	34727	22380	26225	15107	15476	35179	35510
	63-1d2	254684	172195	109037	143391	53014	84419	86688	260500	242352	117373	74779	198475	80478	80400	118699	58560	68925	87556	80649	50265	168234	129455	102910	125521	105472	119346	21535769	6627300	158407	112607	73707	91694	78784	52086	133905	95697
	63-1e2	99816	70045	51454	55386	22968	23631	34483	99452	95850	52560	31214	85773	39766	36455	53925	31796	29446	41881	30779	20978	68465	54488	46247	54344	50965	44660	8615691	2538428	64120	46151	28088	27054	31494	20165	51399	42566
	63-1f2	74276	45376	29234	37126	30928	14592	25895	74451	76932	37529	22993	61639	28517	25918	38331	20886	21254	35649	26072	18774	50398	39944	32400	37559	30060	34849	5932870	1737510	45790	32830	24432	28589	23066	14058	34484	32413
	63-1g2ov	94428	61896	42388	54208	19209	30543	34732	104110	94734	47252	28707	79677	35513	33290	49696	27547	26580	42835	33487	22448	66956	48960	43876	49909	54725	47661	6385274	1886000	59618	40441	35743	32796	28960	18846	49198	40327
	63-1col2	90614	57215	34243	49715	31459	25584	30615	85404	87692	41032	33338	73603	31932	31575	48590	27014	24639	50468	26242	33914	58848	46914	41311	47442	44837	41204	5718259	1696893	57307	39321	32538	30618	25085	16243	38804	34048
<63um	63a2	236362	157861	106731	133652	47208	79263	76483	240098	229314	119948	76974	191205	85469	81407	119585	62861	77190	110953	80013	53108	168634	121758	106022	121378	95822	114690	15186078	4652762	155442	107904	80629	73274	71533	47505	131440	94055
	63b2	115838	76729	51835	64906	43846	36599	39642	120788	114527	52349	36085	95877	48947	40788	60543	33009	36680	64126	37672	24730	77550	61441	52074	60560	56978	50410	8627278	2553167	75337	50991	42406	38320	30447	20855	58088	47202
	63c2	97999	64084	50068	56106	35872	31751	32403	101856	101609	47412	31395	81625	37450	35223	52279	27872	35717	41915	31560	22677	65912	53252	45898	52716	48771	43564	7062562	2085076	62974	43486	29937	28220	29105	20304	49498	38205
	63d2	109332	74403	53472	63070	39901	32917	37937	113945	108762	53307	32617	90675	39772	37308	57762	28773	31237	60816	32489	23790	74921	55662	49578	58678	53082	50666	8445306	2494085	69544	49619	51785	33656	17040	22295	57301	46135
	63-e2	117153	71363	51148	57768	41344	36333	38296	113365	112160	52388	36759	94480	42196	40389	58052	31038	32450	61881	31875	33123	78683	59606	52713	60409	76021	50000	7923832	2327688	69222	48916	48609	34348	30361	21331	64397	47492
	63f2	123351	84984	55441	66137	44228	40192	43924	130292	125002	61064	40340	104032	46529	44466	65643	36603	38715	50498	43750	27182	88988	66126	57798	66700	57950	54282	9079442	2714052	78118	53901	50049	33049	19296	27824	62110	51751
	63g2ov	78454	47960	28968	42867	28432	23250	25081	73764	74760	38801	23384	61326	26266	25933	38062	19706	18311	32186	24498	17495	53620	39356	29200	35380	27385	34124	6402265	1877048	49711	33865	19743	24233	12943	15819	39044	29162
	63col2	123988	83774	54626	70233	42495	33726	42190	125069	120319	56324	39688	100630	46440	42438	63831	34220	39680	65168	37571	34654	83867	63266	55544	64130	57447	52362	8308954	2469106	74821	55078	55709	36383	30901	26848	62444	47703
Initial oil	NS-1	80139	49325	30895	41831	23473	21767	25236	72791	74656	39576	20307	62223	24034	23862	36315	16748	18133	33638	21832	14179	49805	36265	33265	38620	30473	33391	1972134	6826863	50690	33974	23070	24627	24704	13902	35331	31111
	NS-2	99202	66579	50809	52112	40216	29716	26262	93646	94299	46522	28750	71059	32598	31318	47252	24057	28482	42220	29604	20540	64305	44123	41721	48057	38128	43912	2320477	7655506	64215	45792	38558	34073	17142	18454	47754	37258

IV-b: Terpanes (GC-MS Peak Areas)

Terpanes GC peak area																											
		C27Ts	C27Tm	C28 BNH	C29,25n17a-	29,ab30no	C29Ts	C30-DH	C29ba-NH	C30-Ol	C30H	C30ba-H	C31-22S	C31-22R	C31-Gam	C31baS+R	C32-22S	C32-22R	C32baS+R	C33 22S	C33 22R	C34 22S	C34 22R	C35 22S	C35 22R	Int. Std	max191 p.a
Particle size	Sample	Rep1- Migrated oil & col. extract																									
4mm-1mm	1-4a	47525	25556	22454	10796	47200	38613	36905	6502	n.d	121395	22894	63025	49635	16929	24656	55308	42397	30378	45938	31921	27437	16316	29863	19077	8806281	181548
	1-4b	40889	16114	19006	7796	40660	34980	32869	5853	n.d	109833	21371	57819	44550	15677	26470	51108	40376	28395	41659	29718	26280	15939	27256	15977	8583869	178980
	1-4c	65034	32564	32329	14256	69434	57812	56411	13364	n.d	179473	36461	94724	74055	26865	38572	87184	66288	47570	68395	49191	45242	28820	46340	30581	12083815	249182
	1-4d	66912	23427	35274	17083	69814	58427	58703	10624	n.d	183788	38013	100373	78292	28045	41260	88142	68633	47014	75421	56019	47137	32284	54087	32566	12392015	255673
	1-4e	65799	35348	28209	13774	70826	56525	56545	10280	n.d	178035	37133	97505	76728	26904	36970	85232	64699	42522	67814	46353	46011	30123	48600	29963	10969327	230506
	1-4f-ov	45007	25876	22537	12762	53130	40188	41328	7222	n.d	131349	28215	71626	57694	21868	32048	67491	52735	36769	54586	37283	36077	23071	36659	22206	8829131	185536
	1-4g	59725	19671	28394	11071	60909	50887	50170	12511	n.d	160250	33363	87287	69435	24023	36404	78063	60704	42558	64532	43764	43367	27739	45357	28549	9776569	204180
	1-4col	53549	20889	23370	10823	53481	44056	42342	11305	n.d	142214	33042	76192	61680	20350	37598	64621	49866	41969	60884	41332	34808	22562	36460	21906	7193161	152834
1mm-63um	63-1a	52531	23685	24750	9742	55420	45004	43492	8710	n.d	142613	29681	77667	60657	21754	33751	69185	56013	40430	54810	40274	38346	23944	39453	23908	7793957	164499
	63-1b	48904	16521	22867	11382	50857	41922	39957	9899	n.d	133761	27137	71223	55818	19600	29517	62694	50550	35972	52560	35328	33604	24549	37630	22571	8320814	176966
	63-1c	44412	14753	18354	8957	45875	36641	34420	5432	n.d	120658	20441	60479	47991	13800	17988	54227	39500	23007	40502	27357	28873	18589	32540	20981	8591081	179724
	63-1d	39658	14520	18845	9033	41606	34243	34424	5759	n.d	108680	22807	59147	46728	17205	25499	55653	40004	30716	45024	32496	29668	19110	30434	17425	6825292	142338
	63-1e-ov	53932	27881	21212	13170	57916	46395	45814	9130	n.d	149021	30888	78123	62133	21483	33261	75023	55728	39614	56061	41783	39014	27057	40211	25166	7675428	159426
	63-1f	56904	29084	24665	13097	61092	48467	46461	9314	n.d	155097	30246	81727	64529	21393	27498	70304	56058	37358	58215	41363	35535	22459	41154	25057	8680588	183854
	63-1g	45469	24042	20872	9705	47379	39555	37917	9294	n.d	123320	25420	66707	52260	18947	26225	59517	47804	30841	47706	35611	33572	21958	35084	20407	7540425	155793
	63-1col	49448	19121	20389	9427	47842	41242	39606	9866	n.d	133878	29892	69377	57045	18578	34253	68326	48526	33337	53765	35263	30055	20452	34014	20342	7780675	165292
<63um	63a	52758	17439	22990	9267	52628	43704	40866	7169	n.d	136284	25482	69355	54221	17816	27047	60386	47575	29720	47496	32496	30634	20211	33218	19684	9151848	193954
	63b	50219	24989	22681	10898	51082	41879	38293	8220	n.d	129150	24940	68561	52740	17747	26212	60819	47948	31971	48870	34196	30755	20097	31732	19580	8542216	172965
	63c	44217	24318	22764	10503	48016	38816	39436	7925	n.d	122714	25545	65332	51849	19545	28148	58135	46208	31539	49066	35542	33113	21275	34762	21752	6718936	141793
	63d	43369	14898	17256	7147	43408	34967	33200	6839	n.d	110194	20938	58184	44914	15124	23649	51313	39738	29000	42566	29080	25704	17569	27768	16581	7076738	144985
	63e	46991	14818	20602	7153	45607	38724	36803	5969	n.d	121865	23678	64286	50696	17367	25590	58136	45076	30456	48125	33830	30538	18995	31082	19087	7181458	151745
	63f	49274	23268	21507	8490	48564	39403	37467	6652	n.d	125651	22649	64874	50592	14920	21420	55091	41288	24197	42006	29042	29872	19907	33956	20769	7378396	154359
	63gov	49374	23756	22932	11641	54208	43243	42835	7548	n.d	137175	27951	74769	59208	20423	28014	66423	51486	35157	56210	38312	34059	24766	38145	22936	8003767	168046
	63col	58014	18362	27336	12448	56716	46775	45097	8657	n.d	152660	32425	77461	61128	20633	28757	64844	51081	33004	52538	36659	34324	22624	37447	22983	9552335	201255
		Rep2- Migrated oil & col. extract																									
4mm-1mm	1-4a2	48607	31233	29276	17138	41640	40035	40815	9062	n.d	106136	27117	59628	46223	20195	27723	50618	43695	44740	43855	33586	25866	18583	27479	17188	10224316	210178
	1-4b2	42727	14523	17880	7079	41837	33933	33121	6096	n.d	111072	18987	56445	45121	12425	17191	48372	36896	24695	41155	26920	27229	18533	32811	20487	7916351	164686
	1-4c2	52173	26766	23637	11309	54439	43474	44422	10502	n.d	138684	29036	74960	58662	21199	32687	67252	53061	38477	54984	39343	38184	26908	38403	23465	7736972	163053
	1-4d2	42906	14018	18876	9489	44932	36611	35824	5743	n.d	116365	23603	62156	49394	17114	24884	61083	47450	31188	49405	37920	31785	19531	32270	19526	6337269	133868
	1-4e2	47126	14740	20016	8947	48304	39146	37600	7828	n.d	123967	24297	64911	50401	17709	25141	56387	45053	30798	46820	32482	27411	19468	29479	18339	6785763	145434
	1-4f2	53295	17046	24923	10671	54156	45250	42773	8448	n.d	141227	28059	74741	57168	20917	29444	68624	50614	36193	52330	37037	32913	22885	36076	22106	7679101	163752
	1-4g2ov	38380	13367	18343	9075	43376	34305	34469	7066	n.d	111328	23142	60495	49144	17329	24501	54573	44287	32927	45137	32744	30953	19550	31639	17911	5673891	118878
	1-4col2	47202	23069	18809	9526	51363	36812	34401	6870	n.d	122373	22304	60317	48778	13786	23308	53988	39360	22884	41695	26427	29261	18218	32399	20064	5613430	117588
1mm-63um	63-1a2	48670	25589	21776	11164	50555	41167	39814	9338	n.d	129288	26277	69369	54053	18095	26682	60367	48224	33552	49884	34055	32732	20705	33274	20698	7020371	146695
	63-1b2	50762	25752	23799	12405	52210	44605	43178	8355	n.d	141806	28551	74702	58684	20388	27711	67575	52200	35482	52745	40195	34300	23532	36808	21304	7155306	149429
	63-1c2	37948	11582	15619	6909	40038	32001	31441	5120	n.d	104778	18849	54521	42052	14125	22112	49831	36295	24879	39351	26961	24823	16650	29194	17693	7825714	158661
	63-1d2	117762	57115	52800	29425	118470	96762	93805	19715	n.d	306365	59568	154140	120651	40958	57334	131292	95978	59395	101129	71743	66127	42881	73816	47622	21535769	305996
	63-1e2	45504	14439	22406	8554	56308	41510	41761	8188	n.d	131020	27925	72698	57392	21697	30745	64320	53123	39066	56052	40523	35311	26036	38691	22954	8615691	176889
	63-1f2	36775	12539	16461	8153	37966	30662	30844	6086	n.d	96866	20166	53578	42473	15580	22157	48041	38340	29248	40101	29712	26298	18934	27591	16221	5932870	119264
	63-1g2ov	47776	14989	21685	9992	49008	40324	38628	7431	n.d	127082	24188	66989	52070	17953	26642	58672	43732	28446	44696	32015	28223	19628	32751	20645	6385274	134478
	63-1col2	44308	23948	17190	8932	42952	34699	31830	7428	n.d	115511	24955	57154	48134	13965	26705	49223	37968	22883	40934	25837	25405	16381	30222	19036	5718259	120570
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	63b2	54362	23786	27394	14094	58783	46441	46571	9727	n.d	152055	31177	80531	64320	22998	32499	71597	56764	36182	59743	41931	36539	25597	39268	23999	8627278	183230
	63c2	47054	22735	22737	10370	51204	41820	40626	7693	n.d	132195	26730	71220	56749	20238	30454	61907	49800	37109	52985	36581	35905	23908	37455	22413	7062562	140698
	63d2	51161	14314	23450	12290	55792	45143	43659	6031	n.d	141885	28503	76110	59352	21351	32070	64761	52167	33812	55567	36812	33899	23444	35986	21775	8445306	179040
	63-e2	53639	23652	24538	11689	55169	45277	43085	7244	n.d	145830	25850	76225	58636	18104	24111	65553	48196	28212	49205	32766	34609	22859	40008	24723	7923832	160542
	63f2	57293	32300	28443	15301	61647	51874	51082	12315	n.d	163655	35272	88758	70577	25256	36274	78244	64224	41653	62824	41777	42221	27198	45505	27716	9079442	188161
	63g2ov	36596	17113	14706	6272	35291	28142	25847	4064	n.d	90630	14871	45705	35875	10579	14386	39472	29211	16527	29854	19423	20093	12899	22329	14167	6402265	132576
	63col2	57681	16774	27850	11615	57684	49425	46781	11967	n.d	154566	30980	79468	64182	21079	32611	70174	52408	34305	57528	40027	36114	23759	37786	23914	8308954	173220
		N/Sea Crude oil																									
	NS-1	38242	13010	15752	7964	37162	30951	28921	4448	n.d	96585	18630	50426	38874	13358	20054	43710	35015	27771	35249	25898	23810	15379	24297	15966	6826863	140161
	NS-2	40122	20891	17495	9289	40021	32510	30947	4649	n.d	100312	19007	51695	40233	12961	18165	43575	34071	21868	31439	22331	21537	14019	23060	13991	7655506	166951

IV-b: Aromatic HCs (GC-MS Peak Areas)

Aromatic HCs (peak area)																										
Comp.	N	2MN	1MN	BP	2EN	1EN	2-MBP	26+27MN	13+17	16	DPM	14+23	15	12	3-MBP	4-MBP	DBF	137 TMN	136	146+135	236	27+167+12	124	F	125	123	3+2-MF
Ret.Time	14.323	17.43	17.884	19.669	20.048	20.141	20.227	20.335	20.707	20.792	21.053	21.188	21.273	21.581	22.345	22.56	23.063	23.322	23.449	23.819	23.886	24.228	24.618	24.65	24.782	25.185	27.265
Sample	**Rep 1**																										
1-4a	6105821	15804903	12380953	3939317	1879474	663533	647064	10386121	10576407	7903244	362125	3963871	2557569	1615610	3795347	1538887	709667	4219067	5045515	3521896	2684257	4581050	415232	2306860	1165933	312387	1647533
1-4b	5676315	13684683	10377124	3904211	1365654	463866	630196	9741078	8469022	8982920	348970	3997151	2170086	1454606	3690988	1442283	744599	4027933	4905589	4648062	3634319	4337110	364354	2222288	1081895	193765	1563063
1-4c	5461227	16226408	12600369	4399294	1947717	596310	704467	11526430	12542096	9227276	409093	4480254	2586164	1765543	4235032	1680921	850706	4556680	5676658	3913438	2909063	5043844	443763	2562563	1277013	259714	1824536
1-4d	7319463	15389236	11545619	4539108	1353896	472211	711770	10625434	12394115	9439894	401964	3614826	2508001	1639258	4188431	1673451	854143	4861128	5294227	4103684	3315133	4827405	397672	2506097	1217524	215936	1752059
1-4e	7620666	16390476	12373846	5003843	1570801	452199	793198	11896258	12750570	9468814	444469	4938132	2847639	1817763	4698682	1850041	937925	5393601	5988483	7316794	2715285	5426128	453393	2814536	1387828	263867	1990139
1-4f-ov	10925018	20564133	16151707	4617389	2256174	728556	735512	12354338	17762884	7664224	408902	4285937	2561397	1868450	4276511	1754325	906376	4420289	5655521	3992449	3119783	5131851	460473	770163	1286760	298386	1864832
1-4g	7494100	16639674	12716152	4297460	1681413	493235	687971	11139978	12152039	9240247	379744	4616849	2640885	1653769	3963581	1574970	809665	4017766	5276591	4333559	3331166	4673190	399065	2420786	1174575	232616	1692967
1-4col	9228670	20262444	15309363	5051770	2112107	638908	763552	12469899	18409185	7327995	452519	4773596	2830964	1888501	4404580	1782150	903335	5138469	5738960	4102890	3143988	5080460	453130	2766688	1294689	280688	1824339
63-1a	2048773	10103958	7841887	3518691	1114102	377723	609426	9109320	11173703	7538883	347297	3186987	2275178	1408838	3722666	1453083	705753	3864818	4989322	4877629	3652469	4443553	370579	2233942	1125435	236577	1560614
63-1b	3115767	11952719	9258030	3987100	1194669	437553	687010	10050679	12208194	8679985	385703	4315346	2331879	1570186	4067821	1627933	798129	4922391	5491136	3895179	3008262	4887645	408759	2456949	1225202	259029	1787543
63-1c	7267333	18109028	14192193	4295033	2081978	540659	704503	11622070	17065703	6902673	389737	4555960	3034165	1758496	4071177	1643469	836721	4384949	5051608	4065317	3233922	4969019	457125	2495380	1245900	289474	1768381
63-1d	4257620	16673816	12784169	4523167	2015612	657149	738276	12002778	12233913	9168158	424223	4364881	2795854	1846505	4481638	1794909	907458	4121362	5818423	7130773	2685331	5329464	472033	2690592	1335400	277625	1957288
63-1e-ov	4479283	10445595	7610192	4501495	770188	263063	701775	8646836	7233103	7893071	405307	3868399	1932582	1424391	4292934	1694597	851828	4229805	4286962	3270005	2867049	4731467	367746	2576159	1209464	207169	1805728
63-1f	3906335	9142934	6492402	4346241	529646	183038	706071	8082949	7106277	7419524	387213	2966140	1920364	1379487	4134974	1665719	823045	3450672	4798647	6167344	2466461	4729192	359509	2509436	1215756	225979	1758035
63-1g	5785328	11512048	8422310	4176159	898612	304811	647523	8472297	10104924	7419485	363575	2975594	2048020	1375501	3955181	1565272	829036	3656088	4155720	3225281	2844471	4441334	343774	2342523	1115230	222651	1667282
63-1col	10370167	22011444	16622980	7175729	1995709	677409	1049972	15166776	19418489	11748124	635083	7431922	2594283	2505432	6431770	2588601	1466232	5553905	7707105	8614159	3862744	7057042	602854	4074129	1813045	380367	2814540
63a	4708334	15677683	11975033	4686974	1684915	651215	800165	12128382	12637084	10178292	445468	4478143	2730277	1897673	4775068	1926924	946226	4383793	6182080	7701702	2942785	5698238	500493	2866674	1436434	301226	2138116
63b	6418760	15506772	12176729	3882791	1771879	538972	641674	10469163	15574337	6207120	346013	4014681	2555791	1569591	3739046	1482613	731795	3825623	4964087	3700681	2907333	4513239	392088	2215346	1132172	223892	1591783
63c	6546640	16398634	12377862	4953811	1485397	472315	829193	11751907	16832334	7576367	452530	4399345	2465598	1856910	4702576	1890975	934553	4506008	5955578	4213814	3483751	5569326	455848	2762950	1411564	265588	2042294
63d	4565061	10211840	7616871	4677541	663141	223240	763465	7939811	6888620	7121443	467894	3808870	1716613	1468068	4882575	1954476	924720	3347064	4897945	3257622	3437633	5361803	382833	2956126	1363295	292111	2174692
63e	1199340	7774169	5952146	3485971	886012	302059	596691	8023604	9449060	6666036	362852	3550619	1786257	1298068	3823034	1505764	726492	4130460	4685565	3264436	2733681	4396880	342002	2305776	1107076	215213	1677157
63f	2378308	11167759	8706732	3697953	1383662	404470	633343	9444844	9451804	7034851	369098	3119822	2461887	1466587	3867212	1538025	765965	4104358	5074019	3624294	2987895	4605575	387813	2353655	1177610	223189	1710644
63gov	645534	7906419	6119801	3769708	1040913	354895	663553	8739970	7103207	7988563	424599	3879672	2024606	1437599	4423882	1825777	850368	4550006	5218386	3681511	3380892	5195831	403365	2800767	1328548	272300	2104238
63col	3177809	11683723	8560822	5399449	986146	327373	746371	9539252	9904254	7798129	505552	4200412	2204003	1593359	5012260	2049543	1139603	4193776	5084389	6352112	2519691	5104501	381443	3289882	1297901	257629	2241462
	Rep2																										
1-4a2	5961234	17409396	13809262	4566188	1925683	819262	753819	11940512	16241551	9133112	426084	4363372	2748060	1875344	4509600	1804755	848323	4715704	5800184	3977738	3565368	5317602	479358	2730966	1322384	304079	2018390
1-4b2	2988193	12781115	9948332	3534682	1628646	504941	582098	9447746	9548246	7166868	333443	3604469	2304596	1433527	3508497	1386223	598688	4175099	4243002	5727623	2141634	4071772	365181	2099772	1036204	226199	1532157
1-4c2	4797476	14507675	11064863	3770900	1669138	520434	605828	9802871	14598281	5891207	344851	3589225	2192638	1467344	3593341	1427469	725336	4252079	4238610	3344494	2646147	4215249	362912	2156955	1061627	236059	1515211
1-4d2	3574873	11517067	8864609	3686325	1228369	311010	594745	9181630	9824554	7361423	333620	2857066	2414699	1380146	3600250	1452070	734273	3498112	4085727	3247397	2536538	4239317	350554	2189798	1084626	218947	1372189
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1-4f2	2248331	8626701	6558321	3376379	787069	270044	561237	7701609	9415040	6575765	317058	3415352	1699447	1233287	3413349	1355855	671204	3348996	4367292	5409226	1959326	3980423	317075	2050514	1009063	203060	1438589
1-4g2ov	4082794	8786143	6375939	3859909	584654	199229	611720	7109775	7636404	5885184	361633	2980454	1572689	1211413	3802772	1523290	740704	3119371	4119615	3810764	3378380	4120481	305977	2297941	1062485	190353	1621893
1-4col2	2456242	5504712	3936037	3675796	328301	77994	519144	4555239	4393667	3764503	369992	2477634	787784	895926	3728862	1505233	719702	2076156	2995312	3045221	2530967	3528867	228274	2285523	880449	189989	1571585
63-1a2	4962986	10363777	7580361	4838693	701859	240872	801626	8756945	9502126	7172267	456738	4051631	2042719	1552437	4723916	1897325	920559	4384467	4705516	6656186	2736344	5310068	395564	2852823	1362993	141775	2080275
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63-1c2	4475472	10608371	8030764	3383447	1116718	308585	535269	7772205	9165477	6681596	311889	2615256	1918899	1198496	3243329	1304999	654650	3593514	4065586	3389024	2902862	3782688	306547	1979741	954695	128378	1404519
63-1d2	2403528	8438661	6379304	3099997	743937	253488	509188	7239186	8790722	5992375	290903	3180860	1457055	1117696	3133524	1239423	603630	3060546	3981811	1518715	3162000	3609905	284934	1878010	910815	186458	1300228
63-1e2	3676999	12984589	10024371	3525969	1610888	507828	592937	9523754	9750468	7583848	333514	3412710	2089012	1439503	3549476	1392405	699415	3815493	4319547	3205220	2514240	4207643	373591	2128728	1059784	236535	1486727
63-1f2	10050114	21941217	16852242	7102849	2031710	512760	1194693	17315415	25077400	9761861	648373	6284748	4020932	2716637	6820519	2736946	1397034	6940022	8687414	4851919	5743838	7959952	685102	4134706	2030958	433422	2940963
63-1g2ov	3109436	7678098	5751066	3132267	584514	204741	504515	6517761	8020496	5394701	286620	2902249	1411551	1066670	3159148	1261258	624927	2985477	3745320	3420842	2939062	3523966	270235	1875758	910910	178681	1341679
63-1col2	6181812	15196485	10816763	5292600	1021754	282181	800128	11120438	11124770	9563428	482634	4178947	2506934	1838313	4805403	1956593	1061789	4199488	5666886	3843380	3284624	5338922	449227	3117015	1361119	289582	2078290
63a2	1289941	7023815	5420080	2579841	765876	265770	440246	6218634	7562170	5172864	262578	2138962	1541659	986533	2750668	1101048	528278	3087157	3467137	2837745	2339463	3219112	256840	1673365	816780	159019	1197624
63b2	1104360	1506637	1007781	1999373	47156	15962	188748	891219	872222	752104	346339	677840	132340	228115	2413026	1093718	468200	361557	618575	874984	848347	1462546	58664	2124527	325793	102122	1498699
63c2	1296756	8258447	6403074	2848830	1062362	261513	480606	7232680	6026055	6651719	278463	2369850	1706466	1113502	2952211	1175470	570102	3083483	3793285	2695683	2141722	3447967	283730	1762586	887087	180996	1275952
63d2	3860832	10620543	8050690	3075435	1104021	312491	503475	7523464	8899846	6699505	282327	2335509	1973972	1149684	2973854	1187703	592730	3089501	3758089	2877127	2276112	3486720	290251	1787115	891410	184364	1277845
63-e2	1143196	8357573	6541713	3117532	1005765	360029	556487	8089325	8075767	6702944	325927	3475672	1991192	1270329	3337285	1345428	647578	3342589	4406369	3134793	2431592	4005299	335418	2005479	1025455	212630	1480079
63f2	911453	7644046	5893542	2992077	1044888	290853	516889	7589864	8837097	6717423	312081	2554480	1973674	1204296	3232873	1315467	626993	3730729	4223662	2956307	2245058	3869938	317454	1995603	992119	186449	1456517
63g2ov	1265894	6261078	4784509	2545204	586706	208212	426712	5829622	7411851	4531187	258721	2636893	1050129	935244	2717071	1085013	522486	2583060	3431742	1465243	2676506	3150715	251272	1698354	803730	161079	1210480
63col2	1752704	6262897	4564449	3218654	455012	153299	452018	5083336	6550935	3555123	308202	2498104	969518	911192	3146847	1245550	652163	2021598	2899886	2887646	2343852	3186589	218398	1956107	786922	158229	1350456
	Initial oil																										
NS-1	2386511	8895477	6584281	3544505	779606	259121	569397	7591220	9144747	6047009	329437	3353469	1584603	1228864	3554417	1398494	692722	3212685	4193954	1669080	3453011	4031788	316528	2111809	1018288	185818	1513768
NS-2	2239127	12924843	10099705	3968819	1548185	585613	680484	10446364	15264275	6007249	383378	4289862	2705071	1637626	4082936	1644313	809954	3670413	5304279	6564884	2400110	4903815	419216	2458206	1250138	263517	1786898

IV-b: Aromatic HCs (GC-MS Peak Areas) cont'd

Aromatic HCs (peak area)																									
Comp.	1MF	4MF	DBT	P	4MDBT	2+3	1	3MP	2	9	1	4eDBT	4,6DMDBT	2,4 +2,6	1,4	6+(2+3+1E	1,3	,6+35-DM	2,7	)+1,3+2,10	1,6+2,5+2,9	1,7	2,3	,9+4,9+4,1	1,8	
Ret.Time	27.423	27.661	28.416	28.996	30.181	30.515	30.931	31.353	31.467	31.835	31.94	32.368	32.521	32.935	33.41	33.514	33.657	33.679	33.761	34.035	34.155	34.248	34.381	34.477	34.716	36.869
Sample	**Rep1**																									
1-4a	2361323	548917	259718	6595035	48754	1025071	266705	3038516	3475505	4542068	3703153	87287	828425	837914	427319	1068669	239525	1002265	586084	5062663	2649903	1602582	797820	1205234	623725	15012979
1-4b	2221314	513965	191989	6280778	35828	819514	191300	2827228	3202511	5197380	2966657	73838	783381	771750	372273	961350	177576	945506	622628	4509021	2272274	1661462	616741	1086863	558322	14904385
1-4c	2562749	599119	422493	7254909	43809	1231278	306840	3275381	3642473	4915497	3913588	114864	890167	902225	453892	1130338	246752	1092802	699112	6087219	2805532	1941647	699575	1276805	657901	16265014
1-4d	2500997	578261	226994	6989579	46235	911333	226389	3140361	3575185	4808330	3818970	81596	764529	780986	385166	1067179	219061	1153893	709534	5997811	2777928	1859356	699475	1228380	631643	15630365
1-4e	2817907	651316	1306319	7670683	48312	2453326	860810	3510340	3986380	6342002	3931884	243008	1241348	1471451	880834	1239334	406592	1157336	679431	6617477	2909374	1689395	1101837	1095979	687855	16826298
1-4f-ov	2652615	608276	632907	7445214	45545	1624239	456288	3328482	3760851	5009813	4037345	146560	1020974	1078880	577070	1157885	305462	1039464	658002	5322353	3094829	1572691	1035833	1179112	682480	15368630
1-4g	2414198	563495	617515	6652785	42123	1554012	443747	2996003	3405591	5516399	3285486	149358	931219	1019385	551618	1035043	280089	1026342	579279	5658057	2599916	1393229	612199	972832	603200	14987642
1-4col	2734371	617117	942873	7736868	45042	1970645	697868	3344375	3850265	5955314	3787544	175097	1096907	1328914	750437	1154176	375546	1007264	714764	5331582	2250960	1906494	694961	1303496	686192	13469795
63-1a	2326071	536377	1097188	6286951	40227	2057895	724070	2875469	3233199	4452188	3532656	202406	1040226	1245933	745487	1004602	284638	1058014	667739	5477233	2366931	1718318	661318	1147941	597911	14603701
63-1b	2534853	594306	1199181	6915143	43809	2262473	779989	3201309	3529972	4926686	3897105	229739	1114176	1331867	800195	1120508	372016	994322	565688	5522090	2618011	1542010	1066043	985033	655786	15202192
63-1c	2563914	601296	1297375	6948258	43734	2356763	821592	3234340	3591163	4722505	3856661	230314	1122595	1382194	818837	1123013	375276	964386	633398	5300484	2211642	1864642	623389	1285516	630043	15957205
63-1d	2716259	643971	1415523	7571555	53541	2542294	908566	3583633	3808404	6130583	3968472	268789	1206849	1454196	857181	1257115	389417	977729	691201	5710284	2406957	2159390	908182	1264225	679399	15931388
63-1e-ov	2556236	581739	1323574	7195217	42196	2317729	847452	3222728	3681986	5695411	3600008	232606	1129806	1380861	817116	1131251	382858	941690	572226	5886466	2700524	1604587	819882	1137125	629255	14193348
63-1f	2496710	579101	1278493	6953838	41483	2320468	817565	3148544	3542545	4683578	3475129	223731	1101041	1346782	808920	1106827	370315	1351936	467148	5130820	3005286	1525712	954282	1060360	611913	15336547
63-1g	2366782	548417	1181044	6683531	38619	2181461	769289	2929995	3396248	4407920	3668735	210793	1061646	1271530	738059	1030211	349304	835588	559219	4804992	2478768	1421003	938186	978873	576264	14886829
63-1col	3792744	882558	2400470	11835239	64546	3811419	1517962	5623972	5250438	8046973	5949866	379592	1703327	2178793	1246495	1723344	548688	1408912	1017999	8446922	3592774	2807376	1104179	1668568	926454	18646990
63a	2926423	701284	417446	8153619	48173	940188	158143	3682717	4187877	6323657	4352779	106844	575980	417318	213066	1257061	86001	1173604	734340	6119013	3159993	1931225	949265	1364811	740002	15683302
63b	2234118	530295	544759	6222866	37230	1116642	246428	2860296	3180534	4224805	3496201	121994	631092	535288	314454	989036	100918	813414	510042	4694391	2238614	1554855	758402	1000821	575453	12704379
63c	2828105	671007	424913	7521343	46322	1034742	183907	3501551	3959168	6044863	4077733	113287	620992	480084	268249	1127166	102833	979783	671513	5760035	2781289	2062935	1018335	1276820	699677	15449749
63d	2977393	689559	457920	8103640	51728	1056241	203602	3679620	4038852	6488461	4246607	119365	629434	482189	273251	1307722	111122	1175198	654869	6760082	3201975	1842782	684926	1452496	736542	18253683
63e	2378469	552300	331351	6494119	36687	785525	138268	2986965	3359566	5258611	3331477	89944	493920	361995	204112	1028812	76768	951227	584160	5477141	2534902	1406045	895243	1003904	590426	12480428
63f	2410779	565612	380965	6584506	39557	869694	152885	3121295	3408661	4451619	3761113	100799	535558	387731	215115	1029980	83497	822002	558945	4979130	2077940	1492215	594383	1173717	602007	14918094
63gov	2900664	676761	483014	7898525	46807	1105534	202931	3652780	4133408	5344497	4535014	126491	656283	513841	295626	1311624	109904	1105243	675611	5967906	3456707	1814581	555540	1458301	718612	15629238
63col	3073495	689394	903933	9862961	43302	1702027	424513	4186381	4758277	6825054	4936887	162633	826057	777643	416042	1373097	189047	1723140	559683	5951430	2947466	1956123	1110273	1355492	780967	12422732
	Rep2																									
1-4a2	2753237	643317	661652	7688455	53671	1717277	497552	3277091	3753582	5754878	4366726	162120	1069432	1181516	617968	1239543	294806	1034203	693227	5661618	3011527	1812001	598102	1405575	677524	16031130
1-4b2	2097625	495683	637127	5848281	31853	1458749	431657	2651891	3026410	3974849	3260115	137213	839816	933092	510322	906338	258344	1180101	407712	4750683	1768595	1516406	496087	1039842	519928	11719772
1-4c2	2151956	506025	467451	6143306	34320	1267981	350203	2720980	3099333	4049834	3400241	117849	832049	901987	489765	949666	235384	832447	441490	4394082	1872848	1546043	737826	956153	538736	12548338
1-4d2	2211376	513369	389315	6317604	34355	1135452	295913	2786460	3202022	4187569	3491239	103154	819832	885106	430496	982776	202063	827143	521060	5185525	2418014	1331746	859658	981598	560343	13072098
1-4e2	1836036	425621	880361	5274887	30068	1615768	578586	2337147	2660185	3518395	2811937	151928	795092	977757	567406	799471	279011	857122	474285	4417625	1898701	1348591	514402	876962	458377	10507048
1-4f2	2091928	488430	1031191	5866257	35748	1947402	677057	2652146	2982180	4810395	2884545	185263	934434	1144151	672623	935817	310684	802644	564669	4334005	2536857	1254318	537384	865994	539823	11847546
1-4g2ov	2261846	521605	1150621	6407768	37838	2062227	758720	2887852	3214888	4304826	3512215	196024	1015900	1244632	732241	984351	346545	948227	620480	5280951	2456308	1408007	548516	1123353	574735	23683055
1-4col2	2251033	511497	1116161	6150301	35702	1936636	726746	2775457	3115803	4954929	2962244	179256	960703	1182500	702112	954478	341186	903455	588157	5051805	2313934	1597767	769121	892513	544017	10613565
63-1a2	2877967	666215	1427588	7967318	48989	2681138	937711	3684548	4061115	6313428	4304789	271737	1301886	1592589	938090	1322306	440685	1565189	480103	6517218	2616882	2138367	1060501	1331708	726833	16363446
63-1b2	2211704	507179	1057558	6059036	38691	2005656	692432	2753727	3103598	4843279	3057490	196228	964430	1168196	686112	981807	311063	873867	535780	5025918	1853679	1591317	837381	976703	542019	12590491
63-1c2	1990143	460515	936642	5568539	31776	1762335	606731	2517956	2854158	4454055	2753301	173307	878231	1042221	624583	881023	291507	737648	508598	4688452	2111233	1210775	401907	744465	507435	11807001
63-1d2	1914309	436350	912830	5284337	29565	1687680	580115	2390626	2723076	3551413	2960613	166173	833303	1011691	593874	820371	261202	801004	514087	3806662	1989954	1119525	765755	803245	475220	11322707
63-1e2	2132333	515067	1013838	6050554	35814	1940519	641091	2701575	3046171	4667188	3267269	193470	958376	1139952	669985	961528	293356	1131128	432936	4898565	1938493	1397512	756949	1021702	535538	12730748
63-1f2	4065477	962748	2015041	11463905	138418	3716487	1348249	5736289	5657761	9689315	5249617	425602	1860867	2119077	1298141	1989803	606178	1511616	1185737	9944956	4405565	3029567	1179413	1993407	1075669	22267676
63-1g2ov	1873670	428777	985753	5378264	28261	1768305	628913	2467112	2726807	4326010	2570964	179730	842929	1049611	605078	838036	291395	769772	488710	3802275	1980068	1100329	736169	777491	463093	10821110
63-1col2	2887186	681862	1777638	8608723	48936	2808815	1094280	3601798	4037188	5491983	4178578	276211	1270977	1632503	916800	1287843	425650	1490933	568713	5586902	3283491	2081585	926298	1362819	679951	13081010
63a2	1683178	389290	239591	4619389	29365	545277	103357	2129446	2417940	3800021	2318578	61842	332493	251222	146526	736723	56176	618638	392326	4033134	1832266	1025951	411945	713290	432146	9830785
63b2	2146896	487343	256797	5735294	31801	578300	137837	2643326	2994994	4619235	2840736	52768	348939	313194	163960	901080	76431	765028	534876	4209048	2165951	1216369	404526	860139	519918	12220217
63c2	1832565	417377	323261	5003868	30581	719809	141947	2296569	2563727	3331365	2751992	82029	432080	344386	195111	791961	73367	741330	458257	4025580	1732151	1335301	604586	738276	445678	10527523
63d2	1840406	417257	366604	5060547	28946	787173	164032	2284775	2546605	4070337	2489586	85731	439526	362481	209924	784067	83109	714956	447335	4151049	1877271	1363605	376508	888126	455589	10809258
63-e2	2081575	483393	505782	5693334	33284	1077219	250836	2587741	2963934	3828099	3130498	116092	603205	536330	308810	908697	103789	756200	515287	4706032	2180949	1282389	493218	1032443	523460	11712657
63f2	2048229	473209	347101	5545187	32363	789365	141054	2603194	2874894	3767023	3181525	87981	465630	347305	196445	907081	71254	777636	480586	4132728	2004747	1224889	769828	902917	503388	11194535
63g2ov	1722592	392964	324739	4849430	29220	720230	152523	2196149	2458262	3238316	2632832	78405	416639	353376	195977	748690	80793	779326	488978	3966835	1688245	990021	426221	828945	412921	10488105
63col2	1916108	434133	414150	5744893	29740	837361	182544	2509822	2823349	3634784	3050436	85337	450249	374777	214776	813797	88885	846173	527835	4335471	1998975	1120186	706797	771777	467870	8668000
	Initial oil																									
NS-1	2165482	486279	1064705	6022803	35409	1929046	683286	2713634	3110560	4059296	3366338	189120	962579	1166255	684570	951841	322044	833423	491187	5097435	2348821	1285093	536159	1043465	557656	14119138
NS-2	2534997	608103	1247830	7188813	45692	2362339	809339	3214613	3670989	5527878	3787338	232979	1143388	1399783	824026	1070045	370113	1016756	588188	5375687	3060679	1585990	611545	1266852	661556	14620755

IV-b: Aromatic Steroid HCs (GC-MS Peak Areas)

Aromatic Steroid HC GC peak area																					
	21MAS	22MAS	27bS	27dia-S	27bR+	28bS+	28bR+	29aS	28aR+29bF	29aR	253MASpk	TAS20	TAS21	26S	26R+27S	28S	27R	28R	29R	231TASpk	IStd pk
Sample	Rep 1																				
1-4a	161777	196050	34857	226423	238008	421852	534043	87582	332845	44965	430236	204703	220732	45890	163925	113128	109057	102971	22993	3155065	15012979
1-4b	246612	194716	33583	199886	228170	419728	498008	82152	361644	74377	337030	185078	170851	40841	139271	94524	104780	84379	18369	3121177	14904385
1-4c	214816	232086	55502	243225	253012	475110	663834	78023	359216	42262	398358	237792	195087	45287	161560	110502	121864	100050	23558	3427153	16265014
1-4d	290000	245250	79462	250314	287956	523132	826820	144234	460362	102739	396633	214942	181156	46307	159204	107536	104679	93540	23187	3224955	15630365
1-4e	306620	218166	50082	223800	233554	431321	631042	70105	336608	41267	387252	186814	210116	49173	179900	127586	110860	111598	26350	3568418	16826298
1-4f-ov	108540	129823	18364	142395	143903	289439	405607	50447	200979	20772	238385	206759	202971	48083	169640	116041	115779	103331	26626	3237813	15368630
1-4g	306395	215986	49220	225195	232102	439810	648981	92886	316843	34683	390790	182695	174365	39612	146242	101053	94172	90168	21345	3160238	14987642
1-4col	337440	277780	102778	361078	418271	1018962	2335370	600993	1349772	561244	349483	208242	192075	43136	165226	113917	113405	106314	21878	2784876	13469795
63-1a	331742	249530	46507	239553	261107	476629	716081	87652	375486	47945	558960	186503	175438	43406	155486	105523	101988	92349	18728	3084716	16363446
63-1b	279678	225393	48616	232524	240473	454407	663506	92249	348166	38559	410355	206737	192385	48170	173740	119062	117154	103756	27021	3190077	12590491
63-1c	210422	204898	40317	213453	213245	405932	579575	67523	298176	41007	336289	206368	185806	46689	166998	115106	114905	105530	26967	3354678	11807001
63-1d	301380	276317	41339	268049	280898	524137	759047	97971	402471	48465	470279	220388	192644	45336	176793	125617	108066	110347	26332	3277796	11322707
63-1e-d	235562	157649	27643	162778	165892	333494	465366	56745	239732	27375	298282	199011	191349	38219	163934	111785	114486	101893	25100	2980336	12730748
63-1f	199081	149624	33835	151464	137497	289771	408881	58047	223579	39354	263395	208831	184908	43788	158675	111573	88480	97941	23913	3218330	22267676
63-1g	241844	165995	39880	203700	208240	386690	574108	67487	290803	42998	340205	190501	166514	41985	151655	102193	101437	91344	21620	3123581	10821110
63-1col	274785	205517	73054	275493	314579	788270	1805927	586110	935252	429761	1437803	324669	303841	65780	224275	156977	140699	138044	32076	3937759	13081010
63a	336977	262498	44719	275494	293461	542364	758779	102182	390097	51687	454245	224836	232016	50404	200127	134493	122098	121607	25578	3333626	9830785
63b	331010	280966	63057	267695	270826	506430	723681	86219	407032	61800	462456	181691	144877	40428	153773	106654	91771	94923	24405	2626408	12220217
63c	316909	243176	42393	270983	281483	530214	767409	113990	391447	54255	481844	229159	210299	54176	197753	134232	131428	119495	29660	3250272	10527523
63d	239351	168529	24815	179460	162787	324810	445009	55836	244059	26615	317455	247440	208019	53192	194978	135114	121586	121548	31829	3799817	10809258
63e	332206	240614	60438	237294	250478	457934	618875	99219	353401	43638	438224	176672	178774	39010	161362	107294	104193	97109	24654	2629308	11712657
63f	295395	243605	53647	269151	267262	475636	738755	114212	379858	47494	519992	207835	185786	45711	163374	113875	111852	99318	25806	3129247	11194535
63gov	253113	227836	49230	210247	215980	400135	574702	72603	301128	41423	306983	204313	219978	54512	193184	133100	124608	119641	26120	3304781	10488105
63col	167052	120261	41240	139392	156649	368361	746977	180020	432421	146677	634313	209098	193267	43704	150606	102912	102653	93348	19520	2635321	8668000
	Rep 2																				
1-4a2	149625	185338	36137	200500	199388	357660	554706	60915	272562	34884	422098	246551	255013	48328	183559	129984	144908	112092	21852	3359970	16031130
1-4b2	263607	228052	42676	205129	220038	439259	481896	77612	312207	44730	316036	170455	187139	37645	135429	93105	93941	82746	18955	2444876	11719772
1-4c2	277385	244913	56130	266346	271237	521499	619092	96842	388897	42612	475739	185323	169245	39689	140960	99378	95739	87219	20620	2617357	12548338
1-4d2	346547	242952	61266	265617	259543	511858	774580	106138	392967	44397	437397	151130	162132	40334	140585	96109	86377	86071	18144	2767866	13072098
1-4e2	163307	124289	17371	99165	94415	197992	256958	27669	133923	16933	208973	126734	137726	30893	111935	76018	75231	67516	14527	2200964	10507048
1-4f2	310621	252396	54894	239869	239965	454465	679635	90363	353836	46466	456694	183189	164187	38216	132639	92329	89281	79999	18442	2463484	11847546
1-4g2ov	248459	176783	30321	166366	174394	314017	472430	58575	232191	26037	277327	177978	174974	39790	143462	98137	88777	89539	20600	4997508	23683055
1-4col2	130111	102887	16526	117878	108433	262303	509706	130159	286306	76129	81819	169998	174383	35932	132777	87259	79820	79170	15592	2225176	10613565
63-1a2	224196	155545	23851	156601	155105	300456	444284	57932	248025	33418	280795	222791	212585	57068	199172	135877	134968	122871	30416	3448759	14603701
63-1b2	361946	272503	49055	289135	295845	557573	816187	106870	427619	64694	466014	164442	158808	40224	143607	99027	96316	89082	20348	2654955	15202192
63-1c2	276468	204724	49888	221444	237030	458535	662382	82825	361343	52163	379689	170171	148008	35264	127809	89306	80110	78901	17070	2469772	15957205
63-1d2	344112	258967	47388	235065	233559	465188	647223	80532	355646	45726	414155	123788	126912	32949	119415	82644	81581	72614	17481	2350170	15931388
63-1e2	361698	264727	67398	292389	289403	570838	828971	100940	437217	63483	500129	186569	160192	36025	139996	94566	88834	85147	18120	2734228	14193348
63-1f2	360402	258371	48527	262100	272571	510141	760378	109730	400506	51769	465936	384097	361565	80168	261462	181123	155923	153506	34088	4796004	15336547
63-1g2c	350889	271481	53959	271964	290980	556284	841005	96435	429199	45242	516595	141539	133379	34441	121626	84040	73175	73892	15817	2215167	14886829
63-1col	294841	217055	82924	269918	320760	893930	2094436	705394	1177274	541369	1147892	227829	233166	52099	172977	119338	116644	115397	18732	2852394	18646990
63a2	298559	232813	43328	229324	255327	480490	692192	96830	329252	45675	391572	135723	124537	32959	111576	76450	75825	68308	17109	2054978	15683302
63b2 ru	293492	206315	35925	198314	219551	401084	559534	80220	294695	34234	349785	132470	150155	23976	87021	48574	66821	53701	9629	2572483	12704379
63c2	313307	260793	46543	241558	247660	490109	682378	86161	354472	51521	410733	143263	133923	33707	115133	78915	77558	70530	16848	2195906	15449749
63d2	327428	249936	44407	257167	257915	488088	703071	104286	382540	52101	400380	150718	135011	32838	118683	80079	77779	72784	14442	2255551	18253683
63-e2	300792	235593	55939	267015	260393	475560	693353	80702	396155	77341	442176	157000	152600	39326	138627	95102	91850	84159	18641	2453764	12480428
63f2	314839	266755	36615	262947	240755	485953	670936	94721	355950	58306	462035	172134	152296	36551	131942	90460	89037	80544	19184	2340088	14918094
63g2ov	303691	197421	41426	211599	229073	403535	613713	69461	307926	34883	396371	140099	124672	29741	107337	73206	71091	62291	15170	2193589	15629238
63col2	380335	286228	60065	321879	315491	717735	1349001	286399	723016	211749	953978	144954	124191	28973	101958	68686	68559	63222	12614	1805922	12422732
	Initial oil																				
NS-1	171877	137741	30390	140739	142661	284090	393946	48395	203870	28393	218532	184781	163916	40345	140143	95439	87125	80666	16655	2946197	14119138
NS-2	177765	130392	30421	129560	126956	246013	333189	52889	174839	25812	238411	217060	211633	50152	174691	118609	101644	103202	23858	3082624	14620755

IV-b: Saturate HC Data for PCA

		Saturate HCs																											
	For PCA	n-C10	n-C11	n-C12	n-C13	n-C14	n-C15	n-C16	n-C17	Pristane	n-C18	Phytane	n-C19	n-C20	n-C21	n-C22	n-C23	n-C24	n-C25	n-C26	n-C27	n-C28	n-C29	n-C30	n-C31	n-C32	n-C33	n-C34	n-C35	nC36
Sample	Sample code	Normal and isoprenoid alkanes (ppm)																												
1-4a	M1	151	2331	5638	6865	6851	7307	6468	5533	3229	4952	2498	4183	4129	3375	3127	2725	2545	2171	2006	1331	1058	648	509	316	174	55	263	0	0
1-4b	M2	601	3012	6193	7289	7153	7539	6754	5917	3303	5271	2625	4435	4239	3486	3323	2890	2701	2315	2117	1460	1179	753	567	329	192	145	268	0	0
1-4c	M3	533	2706	5980	6948	6898	7318	6576	5719	3128	5098	2544	4293	4226	3454	3292	2916	2738	2304	2188	1445	1155	742	546	355	184	79	152	0	0
1-4d	M4	143	1915	5254	6884	6952	7437	6620	5820	3196	5184	2582	4412	4277	3478	3315	2952	2724	2311	2216	1464	1148	754	568	397	190	69	157	60	64
1-4e	M5	1179	4271	7338	7877	7472	7855	7040	6117	3343	5443	2705	4651	4403	3706	3452	3155	2924	2511	2173	1575	1240	815	603	359	202	75	319	61	41
1-4f-ov	M6	1024	4490	7501	8233	8082	8525	7695	6730	3603	5878	2770	5134	5045	4185	3832	3494	3262	2788	2601	1776	1385	919	674	399	238	74	260	77	85
1-4g	M7	1209	4801	7593	7973	7678	8044	7185	6324	3461	5657	2822	4773	4671	3777	3617	3241	3014	2554	2398	1628	1290	847	651	438	215	88	60	65	85
1-4col	C1	1185	5038	7911	8992	8617	9109	8107	7143	3895	6448	3303	5387	5239	4254	3967	3509	3295	2818	2505	1784	1421	912	691	404	245	139	288	83	83
63-1a	M8	124	727	4295	6868	7502	8230	7431	6598	3618	5977	3104	5013	4888	3991	3681	3228	2995	2570	2274	1725	1432	1000	772	538	283	214	289	63	70
63-1b	M9	191	923	4464	6628	6953	7458	6639	5599	2880	5061	2360	4435	4245	3593	3329	2971	2746	2310	2126	1414	1097	685	511	357	177	124	303	63	0
63-1c	M10	734	3476	6180	7096	7006	7394	6633	5784	3132	5040	2408	4395	4336	3576	3347	2965	2756	2317	2149	1382	1039	627	417	301	152	29	219	53	58
63-1d	M11	99	1821	5009	6549	6681	6869	6524	5737	3107	5178	2527	4425	4356	3594	3351	2970	2745	2361	2081	1417	1093	658	482	281	159	119	183	75	0
63-1e-ov	M12	1010	4351	7008	7866	7546	7951	7022	6122	3357	5431	2699	4539	4278	3555	3390	3021	2781	2361	2192	1470	1137	712	538	374	173	138	250	61	20
63-1f	M13	570	3071	6063	7041	6962	7366	6625	5707	3078	5130	2506	4388	4144	3461	3277	2955	2759	2362	2221	1540	1227	822	629	425	221	152	223	60	67
63-1g	M14	877	3841	6494	7290	7192	7653	6894	6007	3262	5362	2647	4605	4409	3632	3416	3086	2839	2395	2252	1528	1233	833	637	401	236	179	277	60	82
63-1col	C2	571	3145	6306	7438	7334	7722	6907	5998	3249	5297	2588	4540	4412	3686	3447	3173	3049	2758	2693	2002	1646	1182	871	600	336	201	390	75	97
63a	M15	127	1383	4926	6681	6828	7305	6618	5788	3152	5083	2423	4437	4244	3594	3403	3033	2817	2392	2189	1452	1150	743	531	346	179	71	280	60	0
63b	M16	944	4044	6688	7344	7245	7679	6906	6024	3263	5388	2624	4593	4473	3660	3397	3051	2855	2488	2398	1735	1428	991	706	450	260	184	345	68	61
63c	M17	1004	3914	6410	7169	6900	7308	6630	5816	3131	5147	2472	4463	4364	3623	3440	3059	2787	2293	1969	1256	939	517	383	206	129	95	272	59	53
63d	M18	273	2191	5599	7014	7042	7621	6863	6116	3306	5586	2935	4629	4594	3714	3466	3049	2768	2278	2060	1292	976	556	394	258	117	108	264	67	68
63e	M19	131	877	4171	6393	6720	7280	6606	5802	3153	5017	2346	4375	4348	3584	3374	3016	2817	2434	2163	1640	1347	939	715	460	254	192	359	57	73
63f	M20	126	883	4236	6546	6851	7436	6725	5857	3182	5123	2391	4501	4392	3647	3385	2966	2781	2412	2260	1529	1222	811	558	365	198	135	157	68	71
63g-ov	M21	142	197	2687	5651	6573	7325	6696	5880	3168	5208	2521	4463	4370	3605	3394	2943	2798	2390	2206	1521	1206	784	587	375	204	160	293	58	78
63col	C3	117	1678	5253	7035	7173	7707	6947	6096	3304	5353	2554	4608	4411	3668	3520	3189	2960	2585	2452	1727	1400	944	695	475	261	188	172	0	0
1-4a2	R1	496	2488	5436	6595	6654	7141	6460	5778	3060	5197	2507	4466	4400	3691	3541	3114	2918	2513	2253	1570	1247	817	602	400	207	82	286	80	66
1-4b2	R2	106	1924	5345	6911	6949	7408	6670	5836	3127	5242	2524	4438	4392	3609	3467	3100	2877	2449	2328	1557	1226	793	595	393	202	80	265	66	68
1-4c2	R3	448	2835	6265	7492	7454	7846	6932	6088	3292	5397	2660	4598	4468	3649	3448	3051	2872	2464	2284	1563	1239	802	585	392	201	77	267	61	0
1-4d2	R4	379	2478	5981	7246	7260	7692	6889	5931	3199	5337	2646	4577	4370	3715	3448	3100	2832	2434	2040	1546	1224	802	576	383	202	63	282	61	60
1-4e2	R5	107	2116	6126	7753	7688	8114	7150	6267	3399	5553	2743	4685	4613	3858	3584	3130	2952	2496	2347	1605	1277	814	609	353	204	40	332	59	67
1-4f2	R6	104	1417	4781	6809	7047	7553	6744	5906	3207	5199	2566	4550	4459	3679	3434	3055	2820	2357	2241	1543	1214	790	573	346	197	143	263	58	18
1-4g2ov	R7	450	2800	5997	7139	7035	7427	6571	5850	3188	5227	2538	4434	4359	3592	3347	2982	2717	2327	2153	1464	1170	765	566	333	199	154	253	56	66
1-4col2	C4	527	3569	7738	9176	8961	9458	8376	7392	4000	6583	3225	5521	5232	4503	4177	3730	3444	2944	2734	1867	1511	1021	739	478	305	186	310	74	86
63-1a2	R8	733	3665	6357	7190	6941	7355	6561	5702	3062	5166	2513	4429	4381	3646	3379	3031	2828	2439	2332	1675	1405	994	750	503	316	205	283	74	20
63-1b2	R9	107	944	4323	6396	6834	7372	6659	5864	3182	5174	2492	4469	4409	3531	3384	3017	2835	2483	2375	1869	1637	1237	947	614	398	262	374	53	91
63-1c2	R10	645	3088	6047	7201	7112	7547	6781	5916	3213	5156	2391	4529	4393	3580	3424	3038	2846	2484	2412	1758	1501	1088	818	545	308	175	286	57	77
63-1d2	R11	130	980	4335	6524	6897	7333	6492	5895	3185	5217	2433	4496	4415	3604	3365	3045	2829	2446	2306	1518	1177	749	548	323	194	79	293	54	70
63-1e2	R12	117	913	4208	6474	6822	7443	6767	5833	3125	5203	2491	4547	4449	3588	3417	3045	2841	2451	2285	1736	1491	1092	861	568	334	221	313	58	82
63-1f2	R13	529	3001	6297	7175	7108	7510	6736	5871	3188	5245	2550	4524	4432	3662	3405	3064	2819	2447	2347	1635	1387	971	753	495	278	129	297	71	83
63-1g2ov	R14	399	2602	5872	7159	7169	7354	6968	6083	3273	5312	2529	4580	4466	3685	3433	3026	2819	2415	2236	1537	1216	808	561	392	210	67	247	59	57
63-1col2	C5	516	2927	6222	7560	7461	7907	7027	6134	3342	5470	2682	4632	4600	3757	3565	3238	3065	2727	2610	1911	1557	1094	799	539	284	195	297	54	87
63a2	R15	124	508	3599	6164	6735	7275	6614	5815	3136	5191	2521	4483	4278	3589	3413	3043	2810	2407	2025	1401	1058	632	470	276	149	38	259	67	63
63b2	R16	376	2566	5950	7348	7206	7588	6832	5905	3177	5361	2607	4577	4386	3565	3316	3019	2822	2397	2178	1445	1128	692	516	346	138	148	274	53	62
63c2	R17	96	624	4026	6531	6984	7581	6790	5960	3222	5219	2379	4562	4472	3682	3429	2987	2803	2389	2091	1431	1087	644	480	303	158	45	171	64	54
63d2	R18	286	2093	5495	6950	7012	7514	6780	5927	3208	5203	2432	4543	4485	3656	3452	3010	2828	2386	2007	1402	1044	624	447	273	136	35	242	67	72
63-e2	R19	115	608	3925	6402	6798	7061	6710	5849	3180	5146	2455	4490	4368	3693	3433	3043	2793	2388	2143	1416	1068	635	469	280	141	123	234	56	75
63f2	R20	104	361	3242	5996	6642	7344	6703	5801	3119	5242	2598	4525	4344	3631	3411	3067	2817	2403	2213	1450	1097	653	477	295	158	124	135	75	56
63g2-ov	R21	114	846	4081	6607	6981	7562	6775	5832	3151	5299	2630	4536	4433	3660	3403	2974	2804	2460	2291	1564	1251	811	605	417	200	149	148	68	70
63col2	C6	102	1207	5102	7318	7497	7993	7088	6223	3382	5514	2691	4730	4592	3888	3599	3205	2977	2541	2209	1640	1311	849	636	424	216	41	177	62	102
1mm-4mm	E1	34	0	17	74	85	142	142	182	433	120	575	114	85	171	91	399	63	177	91	125	80	80	103	120	68	74	0	0	0
1-63um(1)	E2	44	0	34	97	112	195	170	214	501	136	657	127	107	219	97	428	58	185	93	131	83	68	107	141	83	24	0	0	0
<63um(1)	E3	35	0	35	90	105	191	164	210	467	136	631	129	109	230	101	432	70	191	94	132	86	101	121	125	78	27	0	0	0
1mm-4mm	E4	31	0	26	21	105	173	162	204	482	131	644	126	94	189	100	445	73	199	100	136	89	100	110	147	84	31	0	0	0
1-63um(2)	E5	34	0	46	103	109	172	154	194	457	126	600	114	97	177	86	389	57	166	63	114	69	63	91	86	69	23	0	0	0
<63um(2)	E6	31	0	18	67	94	166	162	211	472	144	647	130	108	225	103	454	76	202	94	144	90	90	112	157	81	31	0	0	0
NS-1	O1	111	1276	4755	6633	6728	6907	6572	5795	3159	5180	2569	4390	4189	3541	3261	2952	2729	2344	2244	1491	1178	800	591	388	209	149	273	58	0
NS-2	O2	152	602	3629	5969	6574	7162	6497	5680	3070	4940	2470	4408	4346	3595	3357	2984	2772	2350	2162	1489	1171	785	562	335	203	68	243	55	20

IV-b: Saturate HC Data for PCA cont'd

		Saturate HC																						
	For PCA	C27Ts	C27Tm	28,30-BNH	C29,25-NH	C29,abNH	C29Ts	C30*DH	C29ba-NH	C30H	C30ba-H	C31-22S	C31 22R	Gamm	C31baS+R	C32 22S	C32R	C32baS+R	C33 22S	C33 22R	C34 22S	C34 22R	C35 22S	C35 22R	Tot.Terp
Sample	Sample code	Terpanes (ppm)																							
1-4a	M1	61	33	29	14	60	49	47	8	155	29	80	63	22	31	70	54	39	59	41	35	21	38	24	1061
1-4b	M2	72	29	34	14	72	62	58	10	195	38	102	79	28	47	91	72	50	74	53	47	28	48	28	1330
1-4c	M3	72	36	36	16	77	64	63	15	200	41	106	82	30	43	97	74	53	76	55	50	32	52	34	1405
1-4d	M4	78	27	41	20	82	68	69	12	215	44	117	92	33	48	103	80	55	88	65	55	38	63	38	1533
1-4e	M5	74	40	32	15	79	63	63	12	200	42	109	86	30	41	96	73	48	76	52	52	34	55	34	1405
1-4f-ov	M6	58	33	29	16	69	52	53	9	170	36	93	75	28	41	87	68	48	71	48	47	30	47	29	1238
1-4g	M7	80	26	38	15	82	68	67	17	216	45	117	93	32	49	105	82	57	87	59	58	37	61	38	1531
1-4col	C1	83	32	36	17	82	68	65	17	219	51	117	95	31	58	100	77	65	94	64	54	35	56	34	1549
63-1a	M8	89	40	42	17	94	77	74	15	243	51	132	103	37	57	118	95	69	93	69	65	41	67	41	1730
63-1b	M9	72	24	34	17	75	62	59	15	198	40	105	82	29	44	93	75	53	78	52	50	36	56	33	1381
63-1c	M10	70	23	29	14	73	58	55	9	191	32	96	76	22	29	86	63	36	64	43	46	29	52	33	1230
63-1d	M11	65	24	31	15	69	57	57	10	179	38	98	77	28	42	92	66	51	74	54	49	32	50	29	1285
63-1e-ov	M12	80	41	31	19	86	69	68	13	220	46	115	92	32	49	111	82	59	83	62	58	40	59	37	1551
63-1f	M13	80	41	35	18	86	68	65	13	218	43	115	91	30	39	99	79	53	82	58	50	32	58	35	1487
63-1g	M14	82	43	38	17	85	71	68	17	222	46	120	94	34	47	107	86	56	86	64	60	40	63	37	1583
63-1col	C2	70	27	29	13	68	58	56	14	189	42	98	81	26	48	97	69	47	76	50	42	29	48	29	1305
63a	M15	68	23	30	12	68	57	53	9	176	33	90	70	23	35	78	62	38	61	42	40	26	43	25	1162
63b	M16	72	36	33	16	73	60	55	12	185	36	98	76	25	38	87	69	46	70	49	44	29	46	28	1282
63c	M17	64	35	33	15	69	56	57	11	177	37	94	75	28	41	84	67	45	71	51	48	31	50	31	1269
63d	M18	77	26	31	13	77	62	59	12	195	37	103	79	27	42	91	70	51	75	51	45	31	49	29	1333
63e	M19	74	23	32	11	72	61	58	9	192	37	101	80	27	40	92	71	48	76	53	48	30	49	30	1316
63f	M20	79	37	34	14	78	63	60	11	201	36	104	81	24	34	88	66	39	67	46	48	32	54	33	1329
63g-ov	M21	67	32	31	16	73	58	58	10	185	38	101	80	28	38	90	69	47	76	52	46	33	51	31	1309
63col	C3	72	23	34	15	70	58	56	11	188	40	95	75	25	35	80	63	41	65	45	42	28	46	28	1235
1-4a2	R1	79	51	48	28	68	65	66	15	173	44	97	75	33	45	82	71	73	71	55	42	30	45	28	1382
1-4b2	R2	82	28	34	14	80	65	63	12	212	36	108	86	24	33	92	70	47	79	51	52	35	63	39	1405
1-4c2	R3	95	49	43	21	100	80	81	19	254	53	137	107	39	60	123	97	70	101	72	70	49	70	43	1834
1-4d2	R4	96	31	42	21	100	82	80	13	260	53	139	110	38	56	137	106	70	110	85	71	44	72	44	1861
1-4e2	R5	91	29	39	17	94	76	73	15	240	47	126	98	34	49	109	87	60	91	63	53	38	57	36	1621
1-4f2	R6	92	29	43	18	93	78	74	15	243	48	129	98	36	51	118	87	62	90	64	57	39	62	38	1664
1-4g2ov	R7	93	33	45	22	106	83	84	17	271	56	147	120	42	60	133	108	80	110	80	75	48	77	44	1932
1-4col2	C4	105	51	42	21	114	82	77	15	272	50	134	109	31	52	120	88	51	93	59	65	41	72	45	1788
63-1a2	R8	88	46	39	20	91	74	72	17	233	47	125	98	33	48	109	87	61	90	62	59	37	60	37	1635
63-1b2	R9	94	48	44	23	97	83	80	15	263	53	139	109	38	51	125	97	66	98	75	64	44	68	40	1812
63-1c2	R10	90	27	37	16	95	76	74	12	248	45	129	100	33	52	118	86	59	93	64	59	39	69	42	1663
63-1d2	R11	95	46	42	24	95	78	75	16	246	48	124	97	33	46	105	77	48	81	58	53	34	59	38	1617
63-1e2	R12	86	27	42	16	106	78	79	15	247	53	137	108	41	58	121	100	74	106	76	67	49	73	43	1804
63-1f2	R13	94	32	42	21	97	78	79	16	247	51	137	108	40	57	123	98	75	102	76	67	48	70	41	1797
63-1g2ov	R14	99	31	45	21	101	83	80	15	263	50	139	108	37	55	121	90	59	92	66	58	41	68	43	1765
63-1col2	C5	101	55	39	20	98	79	72	17	263	57	130	110	32	61	112	86	52	93	59	58	37	69	43	1743
63a2	R15	88	45	43	20	89	74	72	15	230	46	120	94	37	51	105	80	52	79	59	52	37	60	39	1586
63b2	R16	92	40	47	24	100	79	79	17	259	53	137	109	39	55	122	97	62	102	71	62	44	67	41	1797
63c2	R17	91	44	44	20	99	81	79	15	256	52	138	110	39	59	120	96	72	103	71	70	46	73	43	1821
63d2	R18	90	25	41	22	98	80	77	11	250	50	134	105	38	57	114	92	60	98	65	60	41	64	38	1711
63-e2	R19	95	42	44	21	98	80	76	13	259	46	135	104	32	43	116	85	50	87	58	61	41	71	44	1701
63f2	R20	92	52	46	25	99	84	82	20	264	57	143	114	41	58	126	103	67	101	67	68	44	73	45	1871
63g2-ov	R21	88	41	35	15	85	68	62	10	218	36	110	86	25	35	95	70	40	72	47	48	31	54	34	1405
63col2	C6	97	28	47	20	97	83	79	20	260	52	134	108	35	55	118	88	58	97	67	61	40	64	40	1747
1mm-4mm	E1	32	92	30	0	240	45	11	45	124	154	39	95	118	145	18	29	30	0	24	4	11	21	12	1748
1-63um(1)	E2	43	98	33	0	242	65	11	50	134	146	41	104	129	165	17	31	33	0	19	5	11	23	12	1920
<63um(1)	E3	36	97	24	0	271	68	10	50	141	136	40	109	129	166	15	33	27	0	19	5	12	29	16	1953
1mm-4mm	E4	39	108	35	0	284	55	11	53	143	217	47	113	139	177	19	33	34	0	29	5	15	27	14	2005
1-63um(2)	E5	31	89	22	0	250	55	12	47	125	121	39	97	119	154	17	30	32	0	24	5	9	23	11	1779
<63um(2)	E6	35	94	23	0	257	63	11	47	135	144	43	102	125	143	15	32	29	0	18	4	7	18	11	1874
NS-1	O1	89	30	37	18	86	72	67	10	224	43	117	90	31	47	101	81	64	82	60	55	36	56	37	1535
NS-2	O2	70	36	30	16	69	56	54	8	174	33	90	70	22	31	76	59	38	55	39	37	24	40	24	1151

IV-b: Saturate HC Data for PCA cont'd

		Saturate HC																						
	For PCA	C27-20S	C27-20R	C28-S(a)	C28-S(b)	C28-R(a)	C28-R(b)	C29-20S?	C29-20R?	Tot.diast	C27aaa20S	C27bb20R	C27bb20S	C27aa20R	C28aa20S	C28bb20R	C28bb20S	C28aa20R	C29aa20S	C29bb20R	C29bb20S	C29aa20R	Tot.Ster	Ster+Diast.
Sample	Sample code	Diasteranes (ppm)									Steranes (ppm)													ppm
1-4a	M1	141	84	61	80	36	47	137	115	702	48	140	67	42	47	48	69	39	41	70	47	42	701	1403
1-4b	M2	157	100	67	88	25	35	148	124	744	49	153	70	44	57	53	78	48	43	58	52	42	745	1489
1-4c	M3	154	97	81	78	37	34	147	125	753	51	152	71	44	57	52	78	42	45	75	51	39	757	1510
1-4d	M4	158	104	84	79	36	50	152	128	790	53	168	74	47	57	54	79	42	46	77	51	48	795	1585
1-4e	M5	155	94	60	84	40	33	152	127	745	52	156	103	45	56	54	78	41	47	79	51	39	801	1546
1-4f-ov	M6	135	96	72	69	34	44	133	115	698	48	139	80	43	75	47	71	36	42	52	46	40	719	1417
1-4g	M7	154	104	72	78	50	60	153	129	798	53	162	76	46	58	55	82	45	49	85	55	39	806	1604
1-4col	C1	155	102	89	82	53	64	160	132	836	59	163	79	62	59	57	88	49	49	83	52	48	848	1685
63-1a	M8	162	101	90	83	53	44	155	133	821	53	164	81	50	62	58	85	54	88	58	65	58	875	1696
63-1b	M9	146	98	80	71	24	43	147	123	732	48	148	81	44	51	47	72	32	33	48	39	40	682	1414
63-1c	M10	149	92	65	81	21	43	146	120	718	51	145	74	47	57	52	77	41	48	79	53	37	762	1480
63-1d	M11	139	95	58	76	42	37	140	119	706	50	146	70	43	58	51	76	40	43	76	47	37	738	1444
63-1e-ov	M12	158	105	70	89	53	46	155	130	807	52	152	82	50	61	55	83	43	49	62	57	44	790	1597
63-1f	M13	158	101	84	81	52	66	148	127	817	54	158	79	51	58	55	81	42	47	81	53	41	800	1617
63-1g	M14	166	105	72	90	51	43	158	133	818	48	158	86	50	60	56	85	44	49	61	57	47	801	1618
63-1col	C2	154	99	59	84	35	51	146	121	748	50	156	71	52	51	50	73	34	34	63	39	40	713	1461
63a	M15	140	89	72	76	30	33	141	115	696	47	155	71	46	53	51	73	40	54	70	48	35	742	1438
63b	M16	155	103	84	82	33	49	146	124	777	43	144	74	45	52	51	76	40	39	72	51	42	728	1505
63c	M17	153	105	66	85	63	46	146	126	791	51	149	74	43	52	50	76	39	44	69	48	34	730	1521
63d	M18	155	97	77	72	36	48	147	125	757	52	158	75	46	57	53	79	43	41	72	51	38	764	1521
63e	M19	156	96	83	80	35	50	150	127	777	46	162	75	45	56	53	78	44	44	54	54	45	757	1534
63f	M20	159	100	84	84	65	49	157	128	826	54	162	84	49	58	55	80	43	45	75	52	46	802	1629
63g-ov	M21	155	95	58	86	58	46	149	126	772	48	157	72	44	48	50	76	36	43	70	51	32	727	1499
63col	C3	159	107	70	90	56	46	152	125	806	54	165	79	64	54	54	81	45	53	63	46	45	803	1609
1-4a2	R1	161	105	69	88	46	61	149	124	803	53	157	86	47	54	51	77	41	47	81	53	54	799	1602
1-4b2	R2	184	117	79	102	41	39	167	148	876	62	178	82	50	58	57	88	38	40	58	50	48	808	1684
1-4c2	R3	193	121	102	102	60	80	193	163	1014	73	208	99	58	72	67	98	54	52	97	67	48	991	2005
1-4d2	R4	196	134	106	103	68	79	187	160	1032	68	197	96	57	72	67	101	52	55	99	68	45	978	2010
1-4e2	R5	192	115	71	101	49	47	185	157	917	61	195	89	54	64	64	94	49	53	88	62	52	924	1841
1-4f2	R6	198	130	100	103	47	68	184	156	986	65	182	88	54	65	66	96	54	55	89	69	42	925	1911
1-4g2ov	R7	195	117	91	88	55	76	172	156	951	69	205	92	63	91	68	102	56	58	76	75	50	1006	1957
1-4col2	C4	209	129	106	110	86	64	205	170	1078	72	211	140	66	79	73	106	59	60	103	70	53	1095	2173
63-1a2	R8	196	124	100	106	42	45	197	161	971	68	186	98	60	73	68	99	52	67	85	62	47	964	1935
63-1b2	R9	192	122	99	103	44	43	179	157	939	64	197	95	61	71	67	101	54	51	114	55	56	985	1924
63-1c2	R10	191	120	73	105	79	59	195	158	980	63	194	131	55	70	66	99	54	56	99	66	60	1014	1994
63-1d2	R11	204	138	88	115	43	68	195	159	1009	70	209	94	60	65	65	95	47	55	70	65	40	935	1944
63-1e2	R12	188	132	97	104	43	45	181	162	953	65	188	99	59	75	69	102	60	56	79	58	40	948	1901
63-1f2	R13	189	116	75	95	79	37	196	157	944	66	190	96	59	73	66	98	53	54	91	66	48	960	1903
63-1g2ov	R14	195	128	88	112	40	63	196	165	986	72	215	98	59	73	69	103	57	55	89	69	46	1005	1992
63-1col2	C5	206	130	78	113	72	58	200	168	1025	70	194	93	76	73	72	111	61	56	115	60	77	1058	2082
63a2	R15	193	129	87	109	39	65	187	156	966	63	196	98	63	70	67	98	51	63	91	65	43	968	1934
63b2	R16	197	130	88	110	75	62	195	163	1021	67	205	89	61	83	69	103	56	62	109	64	42	1013	2033
63c2	R17	190	124	97	109	69	62	197	158	1006	63	197	92	61	73	68	101	54	69	81	61	44	964	1970
63d2	R18	193	131	94	111	70	58	192	160	1011	67	201	94	58	70	66	102	51	55	107	57	42	970	1981
63-e2	R19	208	127	91	102	73	64	199	168	1031	68	201	93	65	75	72	103	55	58	110	57	59	1014	2045
63f2	R20	199	137	89	107	71	65	201	168	1036	71	210	98	65	75	72	106	59	62	81	70	44	1013	2050
63g2-ov	R21	189	115	70	103	68	56	180	148	929	60	177	93	56	63	62	92	47	44	77	59	42	874	1803
63col2	C6	209	141	92	118	71	57	202	169	1059	71	210	95	67	78	71	107	58	67	110	63	58	1055	2115
1mm-4mm	E1	5	6	7	4	6	6	35	36	105	60	43	24	159	42	39	94	102	39	69	25	195	889	994
1-63um(1)	E2	7	6	7	5	3	6	36	41	111	77	42	27	164	43	40	104	114	35	79	38	212	975	1086
<63um(1)	E3	6	6	7	5	4	7	38	43	115	82	44	27	171	50	65	107	117	39	102	30	223	1056	1171
1mm-4mm	E4	8	6	5	4	4	9	42	43	121	82	44	27	173	49	42	112	118	46	85	39	227	1043	1165
1-63um(2)	E5	7	6	7	4	4	7	34	38	105	70	37	24	146	40	36	91	102	37	71	31	190	875	980
<63um(2)	E6	7	7	7	4	6	4	41	44	121	71	40	25	159	46	59	101	112	36	100	38	213	999	1120
NS-1	O1	186	114	72	97	54	51	173	144	892	59	169	92	47	56	55	84	39	42	78	51	33	804	1696
NS-2	O2	172	115	88	90	70	52	163	123	874	46	162	81	50	57	54	82	42	49	73	51	36	782	1656

IV-b: Aromatic HC Data for PCA

		Aromatic hydrocarbons																																
	Sample code	Naph.	2-MN	1-MN	2-EN	1-EN	2,6+2,7-DMN	1,3+1,7-DMN	1,6-DMN	1,4+2,3-DMN	1,5-DMN	1,2-DMN	1,3,7-TMN	1,3,6-TMN	1,4,6+1,3,5-	2,3,6-TMN	1,2,7+1,6,7+1,2,	1,2,4-TMN	1,2,5-TMN	1,2,3-TMN	Phen	3-MP	2-MP	9-MP	1-MP	3,6-DMP	2,6-+3,5-	2,7-DMP	3,10+1,3+2,10+	1,6+2,5+2,9-	1,7-DMP	2,3-DMP	1,9+4,9+4,10-	1,8-DMP	DMP??
Sample	For PCA	Naphthalenes																			Phenanthrenes													
1-4a	M1	457	1182	926	141	50	777	791	591	296	191	121	315	377	263	201	343	31	87	23	493	227	260	340	277	80	75	44	379	198	120	60	90	47	19
1-4b	M2	486	1173	889	117	40	835	726	770	343	186	125	345	420	398	311	372	31	93	17	538	242	274	445	254	82	81	53	386	195	142	53	93	48	19
1-4c	M3	382	1134	880	136	42	805	876	645	313	181	123	318	397	273	203	352	31	89	18	507	229	254	343	273	79	76	49	425	196	136	49	89	46	18
1-4d	M4	526	1107	830	97	34	764	891	679	260	180	118	350	381	295	238	347	29	88	16	503	226	257	346	275	77	83	51	431	200	134	50	88	45	18
1-4e	M5	521	1121	847	107	31	814	872	648	338	195	124	369	410	501	186	371	31	95	18	525	240	273	434	269	85	79	46	453	199	116	75	75	47	19
1-4f-ov	M6	743	1399	1099	154	50	841	1209	521	292	174	127	301	385	272	212	349	31	88	20	507	226	256	341	275	79	71	45	362	211	107	70	80	46	18
1-4g	M7	594	1320	1008	133	39	883	964	733	366	209	131	319	418	344	264	371	32	93	18	528	238	270	437	261	82	81	46	449	206	110	49	77	48	19
1-4col	C1	708	1556	1175	162	49	957	1413	563	366	217	145	394	441	315	241	390	35	99	22	594	257	296	457	291	89	77	55	409	173	146	53	100	53	20
63-1a	M8	157	776	602	86	29	700	858	579	245	175	108	297	383	375	281	341	28	86	18	483	221	248	342	271	77	81	51	421	182	132	51	88	46	18
63-1b	M9	223	854	661	85	31	718	872	620	308	167	112	352	392	278	215	349	29	88	19	494	229	252	352	278	80	71	40	395	187	110	76	70	47	19
63-1c	M10	568	1415	1109	163	42	908	1333	539	356	237	137	343	395	318	253	388	36	97	23	543	253	281	369	301	88	75	49	414	173	146	49	100	49	21
63-1d	M11	301	1181	905	143	47	850	866	649	309	198	131	292	412	505	190	377	33	95	20	536	254	270	434	281	89	69	49	404	170	153	64	90	48	20
63-1e-ov	M12	349	813	592	60	20	673	563	614	301	150	111	329	334	254	223	368	29	94	16	560	251	287	443	280	88	73	45	458	210	125	64	88	49	20
63-1f	M13	331	776	551	45	16	686	603	629	252	163	117	293	407	523	209	401	30	103	19	590	267	301	397	295	94	115	40	435	255	129	81	90	52	22
63-1g	M14	548	1091	798	85	29	803	957	703	282	194	130	346	394	306	269	421	33	106	21	633	278	322	418	348	98	79	53	455	235	135	89	93	55	22
63-1col	C2	819	1738	1313	158	54	1198	1534	928	587	205	198	439	609	680	305	557	48	143	30	935	444	415	636	470	136	111	80	667	284	222	87	132	73	29
63a	M15	289	961	734	103	40	743	775	624	275	167	116	269	379	472	180	349	31	88	18	500	226	257	388	267	77	72	45	375	194	118	58	84	45	19
63b	M16	488	1179	926	135	41	796	1184	472	305	194	119	291	377	281	221	343	30	86	17	473	217	242	321	266	75	62	39	357	170	118	58	76	44	17
63c	M17	426	1066	805	97	31	764	1094	493	286	160	121	293	387	274	226	362	30	92	17	489	228	257	393	265	73	64	44	374	181	134	66	83	45	19
63d	M18	294	657	490	43	14	511	443	458	245	110	94	215	315	210	221	345	25	88	19	521	237	260	418	273	84	76	42	435	206	119	44	93	47	19
63e	M19	91	591	452	67	23	609	718	506	270	136	99	314	356	248	208	334	26	84	16	493	227	255	399	253	78	72	44	416	193	107	68	76	45	19
63f	M20	175	823	642	102	30	696	697	518	230	181	108	302	374	267	220	339	29	87	16	485	230	251	328	277	76	61	41	367	153	110	44	86	44	19
63g-ov	M21	41	500	387	66	22	553	450	506	246	128	91	288	330	233	214	329	26	84	17	500	231	262	338	287	83	70	43	378	219	115	35	92	45	19
63col	C3	386	1421	1041	120	40	1160	1204	948	511	268	194	510	618	772	306	621	46	158	31	1199	509	579	830	600	167	210	68	724	358	238	135	165	95	40
1-4a2	R1	428	1251	993	138	59	858	1167	656	314	198	135	339	417	286	256	382	34	95	22	553	236	270	414	314	89	74	50	407	216	130	43	101	49	21
1-4b2	R2	262	1122	873	143	44	829	838	629	316	202	126	366	372	503	188	357	32	91	20	513	233	266	349	286	80	104	36	417	155	133	44	91	46	19
1-4c2	R3	424	1281	977	147	46	866	1289	520	317	194	130	376	374	295	234	372	32	94	21	543	240	274	358	300	84	74	39	388	165	137	65	84	48	19
1-4d2	R4	295	950	731	101	26	757	810	607	236	199	114	288	337	268	209	350	29	89	18	521	230	264	345	288	81	68	43	428	199	110	71	81	46	19
1-4e2	R5	217	379	266	14	5	266	268	225	153	49	61	141	218	234	201	306	18	76	16	566	251	285	377	302	86	92	51	474	204	145	55	94	49	20
1-4f2	R6	191	732	556	67	23	653	798	558	290	144	105	284	370	459	166	338	27	86	17	497	225	253	408	245	79	68	48	368	215	106	46	73	46	19
1-4g2ov	R7	353	761	552	51	17	616	661	510	258	136	105	270	357	330	292	357	26	92	16	555	250	278	373	304	85	82	54	457	213	122	47	97	50	20
1-4col2	C4	330	739	528	44	10	611	590	505	333	106	120	279	402	409	340	474	31	118	25	825	373	418	665	398	128	121	79	678	311	214	103	120	73	30
63-1a2	R8	323	674	493	46	16	570	618	467	264	133	101	285	306	433	178	345	26	89	9	518	240	264	411	280	86	102	31	424	170	139	69	87	47	21
63-1b2	R9	132	878	676	101	35	784	854	629	323	192	117	305	400	285	222	360	31	91	19	515	234	264	412	260	83	74	46	427	158	135	71	83	46	19
63-1c2	R10	419	994	753	105	29	728	859	626	245	180	112	337	381	318	272	354	29	89	12	522	236	267	417	258	83	69	48	439	198	113	38	70	48	19
63-1d2	R11	241	845	639	74	25	725	880	600	318	146	112	306	399	152	317	361	29	91	19	529	239	273	355	296	82	80	51	381	199	112	77	80	48	19
63-1e2	R12	330	1164	899	144	46	854	874	680	306	187	129	342	387	287	225	377	34	95	21	543	242	273	419	293	86	101	39	439	174	125	68	92	48	20
63-1f2	R13	471	1028	789	95	24	811	1175	457	294	188	127	325	407	227	269	373	32	95	20	537	269	265	454	246	93	71	56	466	206	142	55	93	50	20
63-1g2ov	R14	314	776	581	59	21	659	810	545	293	143	108	302	378	346	297	356	27	92	18	543	249	276	437	260	85	78	49	384	200	111	74	79	47	20
63-1col2	C5	488	1199	854	81	22	878	878	755	330	198	145	331	447	303	259	421	35	107	23	679	284	319	433	330	102	118	45	441	259	164	73	108	54	22
63a2	R15	138	753	581	82	28	667	811	555	229	165	106	331	372	304	251	345	28	88	17	495	228	259	407	249	79	66	42	432	196	110	44	76	46	19
63b2	R16	97	132	88	4	1	78	76	66	59	12	20	32	54	76	74	128	5	28	9	501	231	262	404	248	79	67	47	368	189	106	35	75	45	19
63c2	R17	134	856	663	110	27	749	624	689	246	177	115	320	393	279	222	357	29	92	19	519	238	266	345	285	82	77	47	417	179	138	63	77	46	19
63d2	R18	400	1100	834	114	32	779	922	694	242	204	119	320	389	298	236	361	30	92	19	524	237	264	422	258	81	74	46	430	194	141	39	92	47	19
63-e2	R19	101	742	581	89	32	718	717	595	308	177	113	297	391	278	216	355	30	91	19	505	230	263	340	278	81	67	46	418	194	114	44	92	46	19
63f2	R20	81	679	523	93	26	674	785	596	227	175	107	331	375	262	199	344	28	88	17	492	231	255	334	282	81	69	43	367	178	109	68	80	45	19
63g2-ov	R21	141	698	533	65	23	650	826	505	294	117	104	288	382	163	298	351	28	90	18	540	245	274	361	293	83	87	54	442	188	110	47	92	46	20
63col2	C6	208	743	542	54	18	603	777	422	296	115	108	240	344	343	278	378	26	93	19	682	298	335	431	362	97	100	63	514	237	133	84	92	56	23
1mm-4m	E1	42	181	273	30	26	111	185	152	68	63	83	42	78	72	20	85	16	35	21	46	15	16	21	26	6	3	3	23	10	6	2	8	5	4
1-63um(	E2	103	287	452	42	36	159	274	209	100	87	117	60	107	99	27	119	23	48	26	57	24	20	29	31	10	5	4	31	12	9	3	9	6	4
<63um(1	E3	121	279	414	35	30	162	261	211	97	85	120	57	111	101	30	125	24	51	31	67	27	23	30	35	11	5	5	34	14	9	3	9	7	4
1mm-4m	E4	88	332	516	62	54	166	305	243	110	104	132	70	121	113	32	136	27	56	33	66	27	23	32	39	13	4	6	36	17	11	3	11	8	6
1-63um(	E5	170	383	579	54	45	180	303	234	106	96	123	64	106	99	28	118	22	47	27	56	24	20	29	31	8	4	4	29	12	8	3	8	6	5
<63um(2	E6	48	190	279	24	21	139	223	183	88	76	112	55	107	98	30	127	24	49	31	71	27	25	34	37	12	4	5	33	15	10	3	11	7	6
NS-1	O1	194	722	534	63	21	616	742	491	272	129	100	261	340	135	280	327	26	83	15	489	220	252	329	273	77	68	40	414	191	104	43	85	45	18
NS-2	O2	159	920	719	110	42	744	1087	428	305	193	117	261	378	467	171	349	30	89	19	512	229	261	393	270	76	72	42	383	218	113	44	90	47	19

IV-b: Aromatic HC Data for PCA cont'd

		Aromatic Hydrocarbons																		Aromatic Steroid HC									
	Sample code	DBT	4-MDBT	3-,+2-MDBT	1-MDBT	4-EDBT??	4,6-DMDBT?	2,4+2,6-DMDBT	1,4-DMDBT	1,3-DMDBT	Biphenyl	2-MB	DPM	3-MB	4-MB	DBF	Fluorene	3-+2-MF	1-MF	4-MF	20TAS	21TAS	22TAS (a+b)	26S TAS	26R+27S TAS	28S TAS	27R TAS	29S TAS (a+b)	28R TAS	29R TAS
Sample	For PCA	Dibenzothiophenes									Biphenyls +other derivatives						Fuorenes				TAS									
1-4a	M1	19	4	77	20	7	62	63	32	18	295	48	27	284	115	53	172	123	177	41	15	17	3	3	12	8	8	4	8	2
1-4b	M2	16	3	70	16	6	67	66	32	15	335	54	30	316	124	64	190	134	190	44	16	15	3	3	12	8	9	3	7	2
1-4c	M3	30	3	86	21	8	62	63	32	17	307	49	29	296	117	59	179	127	179	42	17	14	3	3	11	8	9	3	7	2
1-4d	M4	16	3	66	16	6	55	56	28	16	326	51	29	301	120	61	180	126	180	42	15	13	3	3	11	8	8	3	7	2
1-4e	M5	89	3	168	59	17	85	101	60	28	342	54	30	321	127	64	193	136	193	45	13	14	3	3	12	9	8	4	8	2
1-4f-ov	M6	43	3	111	31	10	69	73	39	21	314	50	28	291	119	62	52	127	180	41	14	14	3	3	12	8	8	3	7	2
1-4g	M7	49	3	123	35	12	74	81	44	22	341	55	30	314	125	64	192	134	191	45	14	14	3	3	12	8	7	3	7	2
1-4col	C1	72	3	151	54	13	84	102	58	29	388	59	35	338	137	69	212	140	210	47	16	15	3	3	13	9	9	3	8	2
63-1a	M8	84	3	158	56	16	80	96	57	22	270	47	27	286	112	54	172	120	179	41	14	13	3	3	12	8	8	3	7	1
63-1b	M9	86	3	162	56	16	80	95	57	27	285	49	28	291	116	57	176	128	181	42	15	14	3	3	12	9	8	3	7	2
63-1c	M10	101	3	184	64	18	88	108	64	29	336	55	30	318	128	65	195	138	200	47	16	15	4	4	13	9	9	4	8	2
63-1d	M11	100	4	180	64	19	85	103	61	28	320	52	30	317	127	64	191	139	192	46	16	14	3	3	13	9	8	4	8	2
63-1e-ov	M12	103	3	180	66	18	88	107	64	30	350	55	32	334	132	66	200	141	199	45	15	15	4	3	13	9	9	3	8	2
63-1f	M13	108	4	197	69	19	93	114	69	31	369	60	33	351	141	70	213	149	212	49	18	16	4	4	13	9	8	4	8	2
63-1g	M14	112	4	207	73	20	101	120	70	33	396	61	34	375	148	79	222	158	224	52	18	16	3	4	14	10	10	4	9	2
63-1col	C2	190	5	301	120	30	135	172	98	43	567	83	50	508	204	116	322	222	300	70	26	24	8	5	18	12	11	5	11	3
63a	M15	26	3	58	10	7	35	26	13	5	287	49	27	293	118	58	176	131	179	43	14	14	3	3	12	8	7	4	7	2
63b	M16	41	3	85	19	9	48	41	24	8	295	49	26	284	113	56	168	121	170	40	14	11	3	3	12	8	7	4	7	2
63c	M17	28	3	67	12	7	40	31	17	7	322	54	29	306	123	61	180	133	184	44	15	14	3	4	13	9	9	4	8	2
63d	M18	29	3	68	13	8	41	31	18	7	301	49	30	314	126	60	190	140	192	44	16	13	3	3	13	9	8	4	8	2
63e	M19	25	3	60	11	7	38	27	16	6	265	45	28	290	114	55	175	127	181	42	13	14	3	3	12	8	8	3	7	2
63f	M20	28	3	64	11	7	39	29	16	6	273	47	27	285	113	56	173	126	178	42	15	14	3	3	12	8	8	3	7	2
63g-ov	M21	31	3	70	13	8	42	33	19	7	239	42	27	280	116	54	177	133	184	43	13	14	3	3	12	8	8	4	8	2
63col	C3	110	5	207	52	20	100	95	51	23	657	91	61	609	249	139	400	273	374	84	25	24	5	5	18	13	12	5	11	2
1-4a2	R1	48	4	123	36	12	77	85	44	21	328	54	31	324	130	61	196	145	198	46	18	18	4	3	13	9	10	3	8	2
1-4b2	R2	56	3	128	38	12	74	82	45	23	310	51	29	308	122	53	184	134	184	44	15	16	3	3	12	8	8	3	7	2
1-4c2	R3	41	3	112	31	10	73	80	43	21	333	54	30	317	126	64	191	134	190	45	16	15	3	4	12	9	8	4	8	2
1-4d2	R4	32	3	94	24	9	68	73	35	17	304	49	28	297	120	61	181	113	182	42	12	13	3	3	12	8	7	4	7	1
1-4e2	R5	94	3	173	62	16	85	105	61	30	298	43	31	323	129	60	198	140	197	46	14	15	3	3	12	8	8	3	7	2
1-4f2	R6	87	3	165	57	16	79	97	57	26	286	48	27	289	115	57	174	122	177	41	16	14	3	3	11	8	8	3	7	2
1-4g2ov	R7	100	3	179	66	17	88	108	63	30	334	53	31	329	132	64	199	140	196	45	15	15	3	3	12	8	8	4	8	2
1-4col2	C4	150	5	260	98	24	129	159	94	46	493	70	50	500	202	97	307	211	302	69	23	23	4	5	18	12	11	5	11	2
63-1a2	R8	93	3	174	61	18	85	104	61	29	315	52	30	307	123	60	186	135	187	43	14	14	3	4	13	9	9	3	8	2
63-1b2	R9	90	3	171	59	17	82	99	58	26	290	50	29	297	121	59	181	132	188	43	14	14	3	3	12	8	8	3	8	2
63-1c2	R10	88	3	165	57	16	82	98	59	27	317	50	29	304	122	61	186	132	186	43	16	14	3	3	12	8	8	3	7	2
63-1d2	R11	91	3	169	58	17	83	101	59	26	310	51	29	314	124	60	188	130	192	44	12	13	3	3	12	8	8	3	7	2
63-1e2	R12	91	3	174	57	17	86	102	60	26	316	53	30	318	125	63	191	133	191	46	17	14	3	3	13	8	8	4	8	2
63-1f2	R13	94	6	174	63	20	87	99	61	28	333	56	30	319	128	65	194	138	190	45	18	17	5	4	12	8	7	3	7	2
63-1g2ov	R14	100	3	179	64	18	85	106	61	29	317	51	29	319	127	63	190	136	189	43	14	13	3	3	12	8	7	4	7	2
63-1col2	C5	140	4	222	86	22	100	129	72	34	418	63	38	379	154	84	246	164	228	54	18	18	4	4	14	9	9	4	9	1
63a2	R15	26	3	58	11	7	36	27	16	6	277	47	28	295	118	57	179	128	180	42	15	13	3	4	12	8	8	4	7	2
63b2	R16	22	3	51	12	5	30	27	14	7	175	16	30	211	96	41	186	131	188	43	12	13	3	2	8	4	6	2	5	1
63c2	R17	33	3	75	15	8	45	36	20	8	295	50	29	306	122	59	183	132	190	43	15	14	3	3	12	8	8	4	7	2
63d2	R18	38	3	82	17	9	46	38	22	9	319	52	29	308	123	61	185	132	191	43	16	14	3	3	12	8	8	3	8	1
63-e2	R19	45	3	96	22	10	54	48	27	9	277	49	29	296	119	57	178	131	185	43	14	14	3	3	12	8	8	3	7	2
63f2	R20	31	3	70	13	8	41	31	17	6	266	46	28	287	117	56	177	129	182	42	15	14	3	3	12	8	8	3	7	2
63g2-ov	R21	36	3	80	17	9	46	39	22	9	284	48	29	303	121	58	189	135	192	44	16	14	3	3	12	8	8	3	7	2
63col2	C6	49	4	99	22	10	53	44	25	11	382	54	37	373	148	77	232	160	227	52	17	15	3	3	12	8	8	4	8	1
1mm-4m	E1	58	2	32	31	3	6	14	43	10	5	4	21	6	3	8	33	21	36	10	1	1	1	2	6	6	3	1	7	1
1-63um(	E2	98	4	50	45	4	9	21	60	12	9	6	29	8	4	11	45	30	50	13	1	2	1	2	8	8	5	3	8	1
<63um(1	E3	75	2	46	44	3	8	20	58	12	11	6	31	10	5	12	46	31	49	14	2	2	1	2	7	7	4	2	8	0
1mm-4m	E4	106	4	48	52	4	9	24	68	15	11	7	33	9	5	13	50	36	58	16	2	3	1	3	10	10	8	2	13	1
1-63um(	E5	87	3	45	44	4	8	19	57	12	9	7	31	9	5	12	44	28	48	13	1	3	2	3	10	11	7	4	12	1
<63um(2	E6	81	1	42	50	4	9	22	66	16	9	6	30	9	5	12	45	32	53	15	2	3	1	3	8	10	6	3	10	1
NS-1	O1	86	3	156	55	15	78	95	56	26	288	46	27	288	113	56	171	123	176	39	15	13	3	3	11	8	7	3	7	1
NS-2	O2	89	3	168	58	17	81	100	59	26	283	48	27	291	117	58	175	127	180	43	15	15	3	4	12	8	7	4	7	2

IV-b: All Biomarkers (Migration Study)

All Biomarkers from Migration Study Samples																		
	Sample	Pr/Ph	Pr/nC17	Ph/nC18	nC17/nC27	CPI-1	CPI-2	CPI-3	DiaSt	St29S/R	St29I/R	27St217	28St217	29St217	St27Iso	St28Iso	St29Iso	St29/Tt30
Crude oil	NS1	1.23	0.55	0.50	3.89	0.90	0.95	0.94	59.59	1.28	1.72	0.66	0.49	0.38	38.80	32.41	28.79	12.79
	NS2	1.24	0.54	0.50	3.81	0.91	0.95	0.94	57.84	1.39	1.47	0.64	0.49	0.39	38.69	32.04	29.27	16.74
	Migrated oils & column extracts Rep1																	
4mm-1mm	1-4a	1.29	0.58	0.50	4.16	0.83	0.92	0.88	52.80	0.99	1.42	0.52	0.46	0.52	37.51	28.51	33.98	18.17
	1-4b	1.26	0.56	0.50	4.05	0.86	0.95	0.90	56.89	1.03	1.28	0.49	0.56	0.46	40.20	31.37	28.43	13.94
	1-4c	1.23	0.55	0.50	3.96	0.87	0.94	0.92	54.40	1.14	1.49	0.53	0.51	0.46	38.59	31.55	29.86	14.88
	1-4d	1.24	0.55	0.50	3.98	0.88	0.95	0.93	54.07	0.96	1.36	0.52	0.44	0.55	38.99	31.17	29.84	14.55
	1-4e	1.24	0.55	0.50	3.88	0.88	0.96	0.93	53.55	1.18	1.51	0.56	0.49	0.45	38.50	31.46	30.04	14.77
	1-4f-ov	1.30	0.54	0.47	3.79	0.89	0.94	0.93	56.16	1.06	1.19	0.57	0.43	0.51	38.24	31.58	30.18	14.61
	1-4g	1.23	0.55	0.50	3.88	0.87	0.97	0.92	53.01	1.26	1.60	0.56	0.52	0.43	37.44	29.48	33.08	14.69
	1-4col	1.18	0.55	0.51	4.00	0.86	0.96	0.91	52.42	1.02	1.39	0.63	0.45	0.44	37.09	31.93	30.98	14.53
1mm-63um	63-1a	1.17	0.55	0.52	3.82	0.91	0.99	0.94	49.41	1.51	0.84	0.44	0.50	0.56	37.44	29.74	32.81	15.18
	63-1b	1.22	0.51	0.47	3.96	0.85	0.95	0.91	60.29	0.83	1.20	0.62	0.38	0.52	37.83	31.46	30.71	11.12
	63-1c	1.30	0.54	0.48	4.18	0.86	0.94	0.93	52.61	1.27	1.56	0.60	0.49	0.43	36.38	29.75	33.87	15.81
	63-1d	1.23	0.54	0.49	4.05	0.84	0.97	0.90	53.49	1.16	1.55	0.56	0.50	0.44	38.51	31.29	30.20	15.75
	63-1e-o	1.24	0.55	0.50	4.16	0.85	0.96	0.91	55.39	1.11	1.28	0.57	0.46	0.47	32.44	33.40	34.16	13.44
	63-1f	1.23	0.54	0.49	3.70	0.89	0.96	0.93	53.90	1.15	1.50	0.61	0.46	0.44	37.56	31.58	30.87	13.98
	63-1g	1.23	0.54	0.49	3.93	0.89	0.95	0.93	55.95	1.04	1.24	0.55	0.46	0.49	38.48	31.28	30.24	13.54
	63-1col	1.26	0.54	0.49	3.00	0.94	0.96	0.96	58.87	0.86	1.37	0.71	0.36	0.47	38.62	31.40	29.97	12.94
<63um	63a	1.30	0.54	0.48	3.99	0.88	0.94	0.93	55.49	1.55	1.32	0.62	0.49	0.41	39.59	31.39	29.01	16.11
	63b	1.24	0.54	0.49	3.47	0.93	0.95	0.95	55.96	0.93	1.51	0.55	0.46	0.49	37.47	31.98	30.55	15.64
	63c	1.27	0.54	0.48	4.63	0.78	0.94	0.86	56.82	1.30	1.50	0.60	0.50	0.41	38.28	31.70	30.02	15.33
	63d	1.13	0.54	0.53	4.73	0.81	0.94	0.89	55.56	1.08	1.55	0.57	0.51	0.43	37.04	31.15	31.81	14.73
	63e	1.34	0.54	0.47	3.54	0.91	0.97	0.94	56.07	0.98	1.21	0.51	0.48	0.50	38.78	31.89	29.33	14.25
	63f	1.33	0.54	0.47	3.83	0.91	0.97	0.95	54.35	0.97	1.41	0.55	0.45	0.50	39.21	32.10	28.69	15.16
	63g-ov	1.26	0.54	0.48	3.87	0.88	0.96	0.92	56.07	1.35	1.63	0.65	0.48	0.39	38.74	32.00	29.26	14.81
	63col	1.29	0.54	0.48	3.53	0.90	0.98	0.94	56.28	1.16	1.12	0.72	0.41	0.42	38.20	29.98	31.82	15.61
	Migrated oils & column extracts Rep2																	
4mm-1mm	1-4a2	1.22	0.53	0.48	3.68	0.88	0.96	0.93	53.21	0.87	1.32	0.49	0.41	0.62	37.17	29.85	32.98	66.83
	1-4b2	1.24	0.54	0.48	3.75	0.87	0.94	0.92	60.62	0.84	1.23	0.58	0.39	0.54	36.35	29.89	33.76	41.20
	1-4c2	1.24	0.54	0.49	3.89	0.88	0.95	0.93	54.33	1.09	1.63	0.56	0.51	0.43	39.33	31.16	29.50	24.97
	1-4d2	1.21	0.54	0.50	3.84	0.89	0.98	0.94	55.18	1.23	1.67	0.59	0.51	0.42	38.50	31.29	30.21	16.17
	1-4e2	1.24	0.54	0.49	3.90	0.86	0.92	0.91	54.58	1.02	1.43	0.54	0.46	0.50	38.45	31.44	30.10	21.79
	1-4f2	1.25	0.54	0.49	3.83	0.89	0.94	0.93	56.30	1.29	1.62	0.56	0.56	0.39	36.41	30.16	33.43	46.69
	1-4g2ov	1.26	0.55	0.49	4.00	0.88	0.95	0.92	54.69	1.16	1.41	0.60	0.49	0.42	37.36	31.30	31.34	18.46
	1-4col2	1.24	0.54	0.49	3.96	0.91	0.95	0.94	54.06	1.13	1.53	0.59	0.49	0.42	37.53	31.63	30.83	33.30
1mm-63um	63-1a2	1.22	0.54	0.49	3.40	0.92	0.95	0.94	55.07	1.43	1.28	0.61	0.49	0.42	37.73	31.22	31.05	43.17
	63-1b2	1.28	0.54	0.48	3.14	0.96	0.96	0.96	53.22	0.92	1.59	0.55	0.46	0.49	37.36	31.52	31.12	45.01
	63-1c2	1.34	0.54	0.46	3.37	0.94	0.95	0.95	52.46	0.93	1.42	0.48	0.47	0.55	38.50	31.68	29.82	42.91
	63-1d2	1.31	0.54	0.47	3.88	0.87	0.93	0.92	59.76	1.37	1.41	0.69	0.47	0.38	39.64	30.42	29.94	400.10
	63-1e2	1.25	0.54	0.48	3.36	0.93	0.96	0.94	57.98	1.40	1.44	0.59	0.61	0.33	38.52	31.52	29.96	44.64
	63-1f2	1.25	0.54	0.49	3.59	0.91	0.93	0.93	54.04	1.13	1.54	0.58	0.50	0.43	40.11	31.06	28.82	21.17
	63-1g2o	1.29	0.54	0.48	3.96	0.91	0.95	0.95	55.50	1.18	1.56	0.57	0.54	0.40	37.14	30.05	32.81	41.66
	63-1col2	1.25	0.54	0.49	3.21	0.93	0.97	0.96	52.22	0.73	1.31	0.55	0.40	0.56	37.70	31.63	30.67	34.95
<63um	63a2	1.24	0.54	0.49	4.15	0.83	0.96	0.89	55.10	1.45	1.47	0.66	0.48	0.38	39.87	31.22	28.90	184.57
	63b2	1.22	0.54	0.49	4.09	0.84	0.96	0.90	54.13	1.48	1.66	0.62	0.54	0.36	38.71	31.37	29.91	63.03
	63c2	1.35	0.54	0.46	4.16	0.82	0.97	0.89	55.14	1.58	1.26	0.62	0.52	0.38	38.43	31.80	29.77	53.52
	63d2	1.32	0.54	0.47	4.23	0.84	0.97	0.91	55.33	1.31	1.70	0.62	0.51	0.39	38.12	31.60	30.28	78.41
	63-e2	1.29	0.54	0.48	4.13	0.83	0.96	0.90	54.20	0.98	1.43	0.57	0.44	0.49	36.64	29.97	33.39	68.27
	63f2	1.20	0.54	0.50	4.00	0.83	0.97	0.90	56.54	1.42	1.43	0.63	0.54	0.35	39.59	31.77	28.64	74.97
	63g2-ov	1.20	0.54	0.50	3.73	0.87	0.98	0.92	57.75	1.05	1.58	0.63	0.48	0.41	42.44	29.48	28.08	25.69
	63col2	1.26	0.54	0.49	3.79	0.87	0.98	0.92	53.99	1.15	1.38	0.58	0.46	0.47	39.07	31.78	29.16	47.89
Rock extract	KCF-1-4	0.75	2.38	4.81	1.45	0.88	1.55	0.99	2.44	0.20	0.40	0.53	0.29	0.75	28.23	31.35	40.42	4.80
	KCF-63-	0.76	2.34	4.82	1.63	0.72	1.40	0.90	3.53	0.16	0.47	0.50	0.30	0.76	27.97	31.91	40.11	4.46
	KCF-<63	0.74	2.22	4.63	1.59	0.98	1.41	1.05	1.89	0.17	0.51	0.50	0.30	0.77	26.91	32.58	40.52	6.48
	KCF-1-4	0.75	2.36	4.92	1.50	1.00	1.47	1.11	3.01	0.20	0.45	0.50	0.29	0.78	26.56	29.90	43.55	4.79
	KCF-63-	0.76	2.35	4.77	1.70	0.79	1.42	0.90	4.68	0.20	0.44	0.50	0.30	0.77	27.13	28.69	44.18	8.88
	KCF-<63	0.73	2.23	4.50	1.47	0.89	1.52	1.04	2.29	0.17	0.56	0.49	0.30	0.79	27.08	32.13	40.79	6.92

IV-b: All Biomarkers (Migration Study) cont'd

All Biomarkers from Migration Study Samples																
Sample	**Ts/Tm**	**BNH**	**29Hops**	**30Hops**	**31Hops**	**25Nor**	**NorH/NorM**	**Hop/Mor**	**Dia/NorM**	**29Ts/29Tm**	**Hop32(S/R)**	**Hop(30/29)**	**HomoHop**	**Hop(35/34)**	**Gam-I**	**Ol-I**
NS1	2.94	0.16	0.20	0.76	0.67	0.08	8.35	5.18	6.50	0.83	1.25	2.60	2.10	1.03	0.14	n.d
NS2	1.92	0.17	0.21	0.76	0.66	0.09	8.61	5.28	6.66	0.81	1.28	2.51	1.84	1.04	0.13	n.d
Migrated oils & column extracts Rep1																
1-4a	1.86	0.1850	0.20	0.76	0.67	0.09	7.26	5.30	5.68	0.82	1.30	2.57	1.96	1.12	0.14	n.d
1-4b	2.54	0.1730	0.19	0.77	0.68	0.07	6.95	5.14	5.62	0.86	1.27	2.70	2.10	1.02	0.14	n.d
1-4c	2.00	0.1801	0.20	0.75	0.68	0.08	5.20	4.92	4.22	0.83	1.32	2.58	2.10	1.04	0.15	n.d
1-4d	2.86	0.1919	0.19	0.74	0.70	0.09	6.57	4.83	5.53	0.84	1.28	2.63	2.28	1.09	0.15	n.d
1-4e	1.86	0.1584	0.20	0.73	0.70	0.08	6.89	4.79	5.50	0.80	1.32	2.51	2.09	1.03	0.15	n.d
1-4f-ov	1.74	0.1716	0.20	0.72	0.70	0.10	7.36	4.66	5.72	0.76	1.28	2.47	2.18	1.00	0.17	n.d
1-4g	3.04	0.1772	0.19	0.74	0.71	0.07	4.87	4.80	4.01	0.84	1.29	2.63	2.28	1.04	0.15	n.d
1-4col	2.56	0.1643	0.19	0.74	0.70	0.08	4.73	4.30	3.75	0.82	1.30	2.66	2.17	1.02	0.14	n.d
63-1a	2.22	0.1735	0.20	0.74	0.70	0.07	6.36	4.80	4.99	0.81	1.24	2.57	2.18	1.02	0.15	n.d
63-1b	2.96	0.1710	0.20	0.75	0.69	0.09	5.14	4.93	4.04	0.82	1.24	2.63	2.22	1.04	0.15	n.d
63-1c	3.01	0.1521	0.20	0.78	0.65	0.07	8.45	5.90	6.34	0.80	1.37	2.63	2.05	1.13	0.11	n.d
63-1d	2.73	0.1734	0.19	0.74	0.70	0.08	7.22	4.77	5.98	0.82	1.39	2.61	2.28	0.98	0.16	n.d
63-1e-ov	1.93	0.1423	0.20	0.75	0.68	0.09	6.34	4.82	5.02	0.80	1.35	2.57	2.13	0.99	0.14	n.d
63-1f	1.96	0.1590	0.20	0.75	0.68	0.08	6.56	5.13	4.99	0.79	1.25	2.54	2.02	1.14	0.14	n.d
63-1g	1.89	0.1693	0.20	0.74	0.70	0.08	5.10	4.85	4.08	0.83	1.25	2.60	2.16	1.00	0.15	n.d
63-1col	2.59	0.1523	0.18	0.77	0.70	0.07	4.85	4.48	4.01	0.86	1.41	2.80	2.18	1.08	0.14	n.d
63a	3.03	0.1687	0.20	0.77	0.65	0.07	7.34	5.35	5.70	0.83	1.27	2.59	2.01	1.04	0.13	n.d
63b	2.01	0.1756	0.20	0.75	0.67	0.08	6.21	5.18	4.66	0.82	1.27	2.53	2.02	1.01	0.14	n.d
63c	1.82	0.1855	0.20	0.74	0.69	0.09	6.06	4.80	4.98	0.81	1.26	2.56	2.14	1.04	0.16	n.d
63d	2.91	0.1566	0.20	0.75	0.67	0.06	6.35	5.26	4.85	0.81	1.29	2.54	2.10	1.02	0.14	n.d
63e	3.17	0.1691	0.19	0.76	0.69	0.06	7.64	5.15	6.17	0.85	1.29	2.67	2.19	1.01	0.14	n.d
63f	2.12	0.1712	0.20	0.77	0.66	0.07	7.30	5.55	5.63	0.81	1.33	2.59	1.96	1.10	0.12	n.d
63g-ov	2.08	0.1672	0.20	0.73	0.70	0.08	7.18	4.91	5.68	0.80	1.29	2.53	2.17	1.04	0.15	n.d
63col	3.16	0.1791	0.19	0.78	0.66	0.08	6.55	4.71	5.21	0.82	1.27	2.69	2.02	1.06	0.14	n.d
Migrated oils & column extracts Rep2																
1-4a2	1.56	0.28	0.20	0.72	0.72	0.16	4.60	3.91	4.50	0.96	1.16	2.55	2.05	1.00	0.19	n.d
1-4b2	2.94	0.16	0.20	0.77	0.66	0.06	6.86	5.85	5.43	0.81	1.31	2.65	2.11	1.16	0.11	n.d
1-4c2	1.95	0.17	0.20	0.74	0.69	0.08	5.18	4.78	4.23	0.80	1.27	2.55	2.16	0.95	0.15	n.d
1-4d2	3.06	0.16	0.20	0.74	0.69	0.08	7.82	4.93	6.24	0.81	1.29	2.59	2.34	1.01	0.15	n.d
1-4e2	3.20	0.16	0.20	0.76	0.67	0.07	6.17	5.10	4.80	0.81	1.25	2.57	2.09	1.02	0.14	n.d
1-4f2	3.13	0.18	0.20	0.76	0.68	0.08	6.41	5.03	5.06	0.84	1.36	2.61	2.14	1.04	0.15	n.d
1-4g2ov	2.87	0.16	0.20	0.73	0.71	0.08	6.14	4.81	4.88	0.79	1.23	2.57	2.30	0.98	0.16	n.d
1-4col2	2.05	0.15	0.22	0.76	0.63	0.08	7.48	5.49	5.01	0.72	1.37	2.38	1.88	1.10	0.11	n.d
63-1a2	1.90	0.17	0.20	0.74	0.69	0.09	5.41	4.92	4.26	0.81	1.25	2.56	2.06	1.01	0.14	n.d
63-1b2	1.97	0.17	0.19	0.76	0.69	0.09	6.25	4.97	5.17	0.85	1.29	2.72	2.10	1.00	0.14	n.d
63-1c2	3.28	0.15	0.20	0.77	0.67	0.07	7.82	5.56	6.14	0.80	1.37	2.62	2.16	1.13	0.13	n.d
63-1d2	2.06	0.17	0.20	0.78	0.65	0.10	6.01	5.14	4.76	0.82	1.37	2.59	1.88	1.11	0.13	n.d
63-1e2	3.15	0.17	0.22	0.70	0.69	0.07	6.88	4.69	5.10	0.74	1.21	2.33	2.32	1.00	0.17	n.d
63-1f2	2.93	0.17	0.20	0.72	0.71	0.08	6.24	4.80	5.07	0.81	1.25	2.55	2.32	0.97	0.16	n.d
63-1g2ov	3.19	0.17	0.20	0.76	0.68	0.08	6.60	5.25	5.20	0.82	1.34	2.59	2.09	1.12	0.14	n.d
63-1col2	1.85	0.15	0.19	0.78	0.66	0.08	5.78	4.63	4.29	0.81	1.30	2.69	1.92	1.18	0.12	n.d
63a2	1.98	0.19	0.20	0.76	0.67	0.09	5.96	5.06	4.86	0.83	1.31	2.60	1.99	1.12	0.16	n.d
63b2	2.29	0.18	0.20	0.75	0.69	0.09	6.04	4.88	4.79	0.79	1.26	2.59	2.13	1.02	0.15	n.d
63c2	2.07	0.17	0.20	0.74	0.70	0.08	6.66	4.95	5.28	0.82	1.24	2.58	2.18	1.00	0.15	n.d
63d2	3.57	0.17	0.20	0.74	0.69	0.09	9.25	4.98	7.24	0.81	1.24	2.54	2.17	1.01	0.15	n.d
63-e2	2.27	0.17	0.20	0.77	0.67	0.08	7.62	5.64	5.95	0.82	1.36	2.64	2.02	1.13	0.12	n.d
63f2	1.77	0.17	0.19	0.74	0.71	0.09	5.01	4.64	4.15	0.84	1.22	2.65	2.13	1.05	0.15	n.d
63g2-ov	2.14	0.16	0.20	0.78	0.65	0.07	8.68	6.09	6.36	0.80	1.35	2.57	1.88	1.11	0.12	n.d
63col2	3.44	0.18	0.19	0.77	0.68	0.08	4.82	4.99	3.91	0.86	1.34	2.68	2.12	1.03	0.14	n.d
KCF-1-4a	0.35	0.24	0.93	0.33	0.37	n.d	5.35	0.80	0.24	0.19	0.62	0.52	0.56	2.12	0.95	n.d
KCF-63-1a	0.36	0.25	0.94	0.32	0.37	n.d	5.40	0.66	0.22	0.20	0.59	0.50	0.56	2.08	0.98	n.d
KCF-<63a	0.44	0.25	0.87	0.35	0.38	n.d	4.83	0.92	0.22	0.27	0.56	0.56	0.56	2.24	0.96	n.d
KCF-1-4b	0.35	0.18	0.96	0.32	0.36	n.d	5.26	1.03	0.24	0.22	0.56	0.50	0.55	2.44	0.95	n.d
KCF-63-1b	0.37	0.17	0.94	0.34	0.36	n.d	5.43	1.04	0.20	0.25	0.46	0.52	0.54	2.67	0.92	n.d
KCF-<63b	0.37	0.17	0.92	0.34	0.37	n.d	5.45	0.94	0.23	0.25	0.46	0.53	0.51	2.77	0.93	n.d

IV-b: All Biomarkers (Migration Study) cont'd

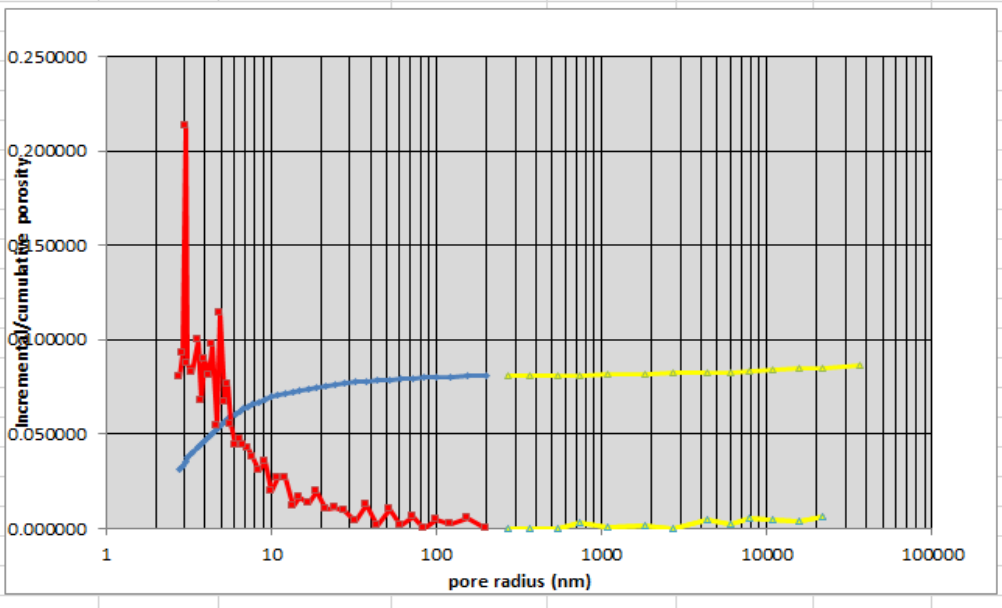
All Biomarkers from Migration Study Samples																							
Sample	MNR	DMNR	MP(3+2/9+1)	MPI(1)	MPI(2)	Rc(Ro<1.35)	Rc(Ro>1.35)	MPR	4/1MDBT	3+2/1MDBT	DBT/PHEN	%R(MDBT)	3/2MeBiph	MAS21+22/tot	MAS29S/R	TAS/MAS	TAS20+21/tot	TAS28S/R	TAS26	TAS27	TAS28	ST	MAS	TAS
NS1	1.35	4.79	0.78	0.65	0.69	0.79	1.91	0.92	0.05	2.82	0.18	0.12	6.24	0.24	1.70	4.70	0.79	1.18	17.45	43.53	39.69	0.27	0.16	1.85
NS2	1.28	3.86	0.74	0.63	0.67	0.78	1.92	0.97	0.06	2.92	0.17	0.15	6.00	0.28	2.05	6.33	0.78	1.15	19.70	42.44	40.45	0.34	0.11	1.81
Migrated oils & column extracts Rep1																								
1-4a	1.28	4.06	0.79	0.66	0.70	0.80	1.90	0.94	0.18	3.84	0.04	0.46	5.87	0.19	1.95	2.04	0.80	1.10	16.82	43.22	40.39	0.34	0.33	1.01
1-4b	1.32	4.49	0.74	0.63	0.67	0.78	1.92	1.08	0.19	4.28	0.03	0.46	5.86	0.23	1.10	2.26	0.77	1.12	13.53	44.76	38.57	0.30	0.31	1.14
1-4c	1.29	4.46	0.78	0.65	0.68	0.79	1.91	0.93	0.14	4.01	0.06	0.39	6.01	0.21	1.85	2.14	0.80	1.10	13.40	44.95	39.04	0.54	0.26	0.80
1-4d	1.33	4.24	0.78	0.65	0.69	0.79	1.91	0.94	0.20	4.03	0.03	0.49	5.88	0.20	1.40	1.55	0.77	1.15	16.66	43.74	39.33	0.55	0.34	0.65
1-4e	1.32	4.18	0.73	0.63	0.67	0.78	1.92	1.01	0.06	2.85	0.17	0.15	5.92	0.26	1.70	2.64	0.69	1.14	17.67	42.78	41.30	0.46	0.23	0.99
1-4f-ov	1.27	4.82	0.78	0.64	0.68	0.79	1.91	0.93	0.10	3.56	0.09	0.30	5.81	0.19	2.43	5.90	0.74	1.12	15.86	43.88	39.68	0.39	0.12	1.60
1-4g	1.31	4.22	0.73	0.62	0.66	0.77	1.93	1.04	0.09	3.50	0.09	0.28	5.76	0.26	2.68	1.87	0.76	1.12	17.04	43.52	40.58	0.45	0.32	0.82
1-4col	1.32	4.40	0.74	0.62	0.66	0.77	1.93	1.02	0.06	2.82	0.12	0.18	5.77	0.09	1.07	0.64	0.74	1.07	16.02	43.98	40.63	0.17	1.09	0.50
63-1a	1.29	4.00	0.77	0.64	0.68	0.79	1.91	0.92	0.06	2.84	0.17	0.14	6.11	0.26	1.83	1.22	0.73	1.14	16.51	44.01	39.67	0.25	0.56	0.78
63-1b	1.29	4.31	0.76	0.64	0.67	0.78	1.92	0.91	0.06	2.90	0.17	0.15	5.92	0.24	2.39	2.06	0.71	1.15	15.57	44.30	39.66	0.25	0.35	1.17
63-1c	1.28	3.83	0.80	0.66	0.69	0.80	1.90	0.93	0.05	2.87	0.19	0.13	5.78	0.22	1.65	2.95	0.71	1.09	16.09	43.53	40.17	0.29	0.24	1.37
63-1d	1.30	4.29	0.73	0.63	0.65	0.78	1.92	0.96	0.06	2.80	0.19	0.16	6.07	0.24	2.02	1.63	0.73	1.14	17.51	43.28	41.68	0.17	0.48	1.12
63-1e-ov	1.37	4.47	0.74	0.63	0.67	0.78	1.92	1.02	0.05	2.73	0.18	0.11	6.12	0.27	2.07	3.58	0.74	1.10	14.44	45.93	40.29	0.35	0.19	1.37
63-1f	1.41	4.21	0.82	0.66	0.70	0.80	1.90	1.02	0.05	2.84	0.18	0.12	5.86	0.26	1.47	4.56	0.79	1.14	20.32	41.71	41.86	0.44	0.14	1.32
63-1g	1.37	4.14	0.78	0.64	0.69	0.79	1.91	0.93	0.05	2.84	0.18	0.12	6.11	0.22	1.57	2.47	0.73	1.12	16.40	44.12	39.61	0.28	0.29	1.26
63-1col	1.32	5.85	0.78	0.63	0.61	0.78	1.92	0.88	0.04	2.51	0.20	0.07	6.13	0.09	1.36	0.38	0.87	1.14	17.92	42.32	40.65	0.07	2.11	0.35
63a	1.31	4.44	0.74	0.63	0.67	0.78	1.92	0.96	0.30	5.95	0.05	0.59	5.97	0.24	1.98	1.88	0.73	1.11	18.37	44.00	40.73	0.30	0.37	1.01
63b	1.27	4.10	0.78	0.65	0.68	0.79	1.91	0.91	0.15	4.53	0.09	0.41	5.83	0.26	1.40	1.16	0.67	1.12	18.68	42.98	41.34	0.33	0.53	0.67
63c	1.32	4.77	0.74	0.63	0.67	0.78	1.92	0.97	0.25	5.63	0.06	0.54	5.67	0.23	2.10	1.75	0.69	1.12	16.37	44.10	39.83	0.19	0.44	1.15
63d	1.34	4.63	0.72	0.61	0.64	0.77	1.93	0.95	0.25	5.19	0.06	0.54	6.40	0.28	2.10	5.12	0.73	1.11	18.04	42.90	40.97	0.19	0.16	2.39
63e	1.31	4.49	0.74	0.63	0.67	0.78	1.92	1.01	0.27	5.68	0.05	0.55	6.41	0.27	2.27	1.44	0.70	1.10	16.75	45.24	40.16	0.26	0.48	0.87
63f	1.28	3.84	0.80	0.66	0.69	0.80	1.90	0.91	0.26	5.69	0.06	0.55	6.11	0.23	2.40	1.37	0.74	1.15	15.13	44.06	39.91	0.22	0.53	0.90
63g-ov	1.29	4.32	0.79	0.66	0.70	0.79	1.91	0.91	0.23	5.45	0.06	0.52	6.67	0.26	1.75	3.61	0.68	1.11	17.45	43.00	40.44	0.29	0.20	1.53
63col	1.36	4.33	0.76	0.62	0.66	0.77	1.93	0.96	0.10	4.01	0.09	0.30	6.72	0.13	1.23	0.93	0.82	1.10	16.45	43.31	39.79	0.41	0.59	0.52
Migrated oils & column extracts Rep2																								
1-4a2	1.26	4.35	0.69	0.59	0.63	0.76	1.94	0.86	0.11	3.45	0.09	0.32	5.98	0.20	1.75	2.87	0.81	1.16	10.32	46.34	39.12	1.12	0.14	0.54
1-4b2	1.28	4.10	0.78	0.65	0.69	0.79	1.91	0.93	0.07	3.38	0.11	0.22	6.03	0.27	1.74	1.88	0.81	1.13	15.21	44.24	39.71	1.24	0.18	0.41
1-4c2	1.31	4.47	0.78	0.64	0.68	0.79	1.91	0.91	0.10	3.62	0.08	0.29	5.93	0.23	2.27	1.13	0.77	1.14	15.46	43.60	40.30	1.07	0.29	0.34
1-4d2	1.30	3.80	0.78	0.64	0.69	0.79	1.91	0.92	0.12	3.84	0.06	0.34	6.05	0.24	2.39	1.18	0.70	1.12	18.79	42.46	40.53	0.74	0.36	0.45
1-4e2	1.42	5.40	0.79	0.65	0.69	0.79	1.91	0.95	0.05	2.79	0.17	0.13	7.53	0.34	1.63	4.51	0.73	1.13	16.07	44.17	39.69	2.02	0.06	0.37
1-4f2	1.32	4.53	0.73	0.62	0.66	0.77	1.93	1.03	0.05	2.88	0.18	0.13	6.08	0.26	1.94	1.08	0.80	1.15	15.68	43.66	39.85	1.27	0.27	0.30
1-4g2ov	1.38	4.52	0.78	0.64	0.68	0.79	1.91	0.92	0.05	2.72	0.18	0.11	6.22	0.29	2.25	5.62	0.77	1.10	18.70	42.62	40.83	0.49	0.11	1.32
1-4col2	1.40	5.78	0.74	0.63	0.66	0.78	1.92	1.05	0.05	2.66	0.18	0.11	7.18	0.15	1.71	7.49	0.83	1.10	19.46	43.38	40.11	1.51	0.05	0.54
63-1a2	1.37	4.29	0.73	0.63	0.66	0.78	1.92	0.94	0.05	2.86	0.18	0.13	5.89	0.27	1.73	5.62	0.67	1.11	16.46	43.47	39.81	0.85	0.09	0.84
63-1b2	1.30	4.08	0.74	0.63	0.67	0.78	1.92	1.02	0.06	2.90	0.17	0.14	5.91	0.24	1.65	1.02	0.69	1.11	16.39	43.51	40.17	0.93	0.35	0.36
63-1c2	1.32	4.05	0.75	0.63	0.67	0.78	1.92	1.04	0.05	2.90	0.17	0.13	6.06	0.23	1.59	1.26	0.77	1.13	17.60	42.97	40.89	1.07	0.27	0.37
63-1d2	1.32	4.97	0.79	0.65	0.69	0.79	1.91	0.92	0.05	2.91	0.17	0.12	6.15	0.29	1.76	1.05	0.64	1.14	15.29	44.20	39.89	8.60	0.05	0.06
63-1e2	1.30	4.56	0.72	0.62	0.65	0.77	1.93	0.93	0.06	3.03	0.17	0.14	5.99	0.24	1.59	0.92	0.78	1.11	17.40	44.18	40.42	0.99	0.35	0.32
63-1f2	1.30	4.31	0.76	0.65	0.64	0.79	1.91	1.08	0.10	2.76	0.18	0.30	5.71	0.26	2.12	3.55	0.90	1.18	18.94	41.99	40.21	0.26	0.21	1.64
63-1g2ov	1.34	4.62	0.75	0.63	0.67	0.78	1.92	1.06	0.04	2.81	0.18	0.09	6.26	0.24	2.13	0.64	0.71	1.14	18.81	42.49	40.79	0.82	0.50	0.27
63-1col2	1.40	4.44	0.79	0.63	0.66	0.78	1.92	0.97	0.04	2.57	0.21	0.09	6.01	0.08	1.30	0.24	0.80	1.03	18.12	41.50	40.72	0.19	2.14	0.19
63a2	1.30	4.03	0.74	0.64	0.68	0.78	1.92	1.04	0.28	5.28	0.05	0.57	6.25	0.24	2.12	0.88	0.71	1.12	16.34	43.26	39.65	6.79	0.07	0.06
63b2	1.50	6.73	0.76	0.64	0.68	0.78	1.92	1.05	0.23	4.20	0.04	0.52	12.78	0.27	2.34	1.13	1.01	0.90	18.05	45.46	36.51	2.26	0.17	0.19
63c2	1.29	4.24	0.80	0.66	0.69	0.79	1.91	0.93	0.22	5.07	0.06	0.50	6.14	0.26	1.67	0.91	0.74	1.12	16.51	43.25	39.76	1.20	0.31	0.28
63d2	1.32	3.81	0.74	0.62	0.66	0.77	1.93	1.02	0.18	4.80	0.07	0.45	5.91	0.25	2.00	0.94	0.75	1.10	17.26	43.60	40.00	1.58	0.25	0.23
63-e2	1.28	4.06	0.80	0.66	0.70	0.79	1.91	0.95	0.13	4.29	0.09	0.37	6.00	0.23	1.04	1.08	0.69	1.13	16.51	43.57	39.92	1.30	0.26	0.29
63f2	1.30	3.85	0.79	0.66	0.69	0.79	1.91	0.90	0.23	5.60	0.06	0.52	6.25	0.26	1.62	0.98	0.76	1.12	15.98	43.97	39.90	1.65	0.23	0.23
63g2-ov	1.31	5.55	0.79	0.65	0.69	0.79	1.91	0.93	0.19	4.72	0.07	0.47	6.37	0.26	1.99	0.99	0.77	1.18	15.58	44.56	39.43	0.93	0.35	0.35
63col2	1.37	5.24	0.80	0.64	0.68	0.79	1.91	0.93	0.16	4.59	0.07	0.43	6.96	0.17	1.35	0.16	0.81	1.09	17.03	43.41	39.80	0.73	1.00	0.09
KCF-1-4a	0.66	1.77	0.67	0.50	0.51	0.70	2.00	0.61	0.06	1.01	1.26	0.17	1.41	0.01	1.23	0.00	0.10	0.79	19.42	28.30	55.61	0.00	105.54	0.00
KCF-63-1a	0.64	1.83	0.73	0.56	0.52	0.74	1.96	0.64	0.08	1.09	1.73	0.23	1.29	0.01	1.23	0.01	0.09	0.94	20.50	32.09	51.83	0.01	83.46	0.01
KCF-<63a	0.67	1.91	0.78	0.57	0.53	0.74	1.96	0.67	0.06	1.04	1.13	0.15	1.52	0.01	1.21	0.01	0.12	0.92	20.09	31.16	53.13	0.01	38.87	0.01
KCF-1-4b	0.64	1.61	0.70	0.55	0.50	0.73	1.97	0.59	0.07	0.93	1.60	0.22	1.30	0.00	1.22	0.01	0.10	0.81	12.92	33.07	52.75	0.00	104.50	0.01
KCF-63-1b	0.66	1.88	0.74	0.57	0.52	0.74	1.96	0.65	0.08	1.01	1.57	0.23	1.30	0.00	1.19	0.02	0.10	0.90	16.87	32.44	52.23	0.02	30.34	0.02
KCF-<63b	0.68	1.83	0.73	0.55	0.53	0.73	1.97	0.67	0.01	0.84	1.14	-0.21	1.44	0.01	1.19	0.01	0.12	1.03	13.77	31.41	54.22	0.01	37.48	0.01

IV-c: Mercury Injection Porosimetry and Particle Density Measurements

MICP ANALYSIS DATA/ RESULT

Date of Analysis	5/21/2012	Sample Depth (m):	n/a	Penetrometer Vol. (ml)	6.0569	Sample Volume (ml)	0.837
Instrument	Penetrometer	Sample Weight (g)	1.1383	Sample+Pen Wt (g)	63.7464	Total Porosity	0.089
Pen.Number/ Type	07-0002 / 5cc solid	Corrected Vol. (ml)	0.831	Sample+Pen+Hg Wt (g)	134.4161	Corrected porosity	0.082
Run conditions set #	1	Samp. bulk Density(g/ml)	1.359	Hg Weight (g)	70.6697	Mean pore radius (nm)	7.76
Sample Name	KCF BlackStone	Corrected Density g/ml)	1.370	Hg Density	13.5399	Particle density, Gs (g/ml	1.492

Ave	Pressure (psi)	Cumulative/incre pore Vol.(ml/g)	Pore Diameter (μm)	Intrusion (micron ml)	Radius (nm)	Accum. Porosity	Corrected Distribu.	mean radius	Density Distribution	Cumulative Distribution	r_{mean} nm	r_{10} nm
0.0000	3	0.0018	72.8895	0.002049	36444.75	0.086576				* above the nearest 90% cell		
0.0000	5	0.0028	43.7337	0.003187	21866.85	0.085217		28229.98196	0.006127			
0.0000	7	0.0032	31.2384	0.003643	15619.2	0.084673		18480.87399	0.003721			
0.0000	10	0.0037	21.8668	0.004212	10933.4	0.083994		13067.93638	0.004387			
0.0000	14	0.0043	15.6192	0.004895	7809.6	0.083178		9240.426432	0.005581			
0.0000	18	0.0045	12.1482	0.005122	6074.1	0.082906		6887.400915	0.002491			
0.0000	25	0.005	8.7467	0.005692	4373.35	0.082227		5154.043581	0.004763			
0.0000	40	0.005	5.4667	0.005692	2733.35	0.082227		3457.440704	0.000000			
0.0000	60	0.0052	3.6445	0.005919	1822.25	0.081955		2231.781136	0.001544			
0.0000	100	0.0053	2.1867	0.006033	1093.35	0.081819		1411.508781	0.000613			
0.0000	150	0.0057	1.4578	0.006488	728.9	0.081275		892.7165368	0.003087			
0.0000	200	0.0057	1.0933	0.006488	546.65	0.081275		631.2314829	0.000000			
0.0000	300	0.0057	0.7289	0.006488	364.45	0.081275		446.3480621	0.000000			
0.0000	400	0.0057	0.5467	0.006488	273.35	0.081275		315.6301752	0.000000			
0.0000	550	0.0057	0.3976	0.006488	198.8	0.081275	0.081910	233.1136633	0.000000	100.0000	7.76	
0.0000	700	0.0061	0.3124	0.006944	156.2	0.080732	0.081362	176.2173658	0.005191	99.3311	6.58	
0.0000	900	0.0063	0.243	0.007171	121.5	0.080460	0.081088	137.7617509	0.002492	98.9966	6.12	
0.0000	1100	0.0066	0.1988	0.007513	99.4	0.080052	0.080677	109.8958598	0.004677	98.4949	5.57	
0.0000	1300	0.0066	0.1682	0.007513	84.1	0.080052	0.080677	91.43052007	0.000000	98.4949	5.57	
0.0000	1500	0.0069	0.1458	0.007854	72.9	0.079644	0.080266	78.3	0.006569	97.9932	5.18	
0.0000	1800	0.007	0.1215	0.007968	60.75	0.079508	0.080129	66.54829074	0.001717	97.8260	5.06	
0.0000	2100	0.0075	0.1041	0.008537	52.05	0.078829	0.079444	56.23199712	0.010124	96.9898	4.59	
0.0000	2500	0.0076	0.0875	0.008651	43.75	0.078693	0.079307	47.71988579	0.001802	96.8226	4.51	
0.0000	2900	0.0082	0.0754	0.009334	37.7	0.077877	0.078485	40.61249808	0.012617	95.8192	4.11	
0.0000	3400	0.0084	0.0643	0.009562	32.15	0.077606	0.078211	34.81458028	0.003931	95.4848	3.99	
0.0000	3900	0.0088	0.0561	0.010017	28.05	0.077062	0.077664	30.03011	0.009176	94.8158	3.79	
0.0000	4500	0.0093	0.0486	0.010586	24.3	0.076382	0.076979	26.10776	0.010904	93.9797	3.57	
0.0000	5100	0.0097	0.0429	0.011042	21.45	0.075839	0.076431	22.83057	0.010035	93.3107	3.42	
0.0000	5800	0.0105	0.0377	0.011952	18.85	0.074751	0.075335	20.10802	0.019377	91.9729	3.15	*
0.0000	6500	0.011	0.0336	0.012521	16.8	0.074072	0.074650	17.79551	0.013591	91.1367	3.00	***14.73***
0.0000	7300	0.0116	0.03	0.013204	15	0.073256	0.073828	15.87451	0.016569	90.1333	2.84	14.8
0.0000	8100	0.012	0.027	0.013660	13.5	0.072712	0.073280	14.23025	0.011882	89.4644	2.75	14.7
0.0000	9000	0.0129	0.0243	0.014684	12.15	0.071489	0.072047	12.80722	0.026734	87.9593	2.55	
0.0000	9900	0.0137	0.0221	0.015595	11.05	0.070402	0.070952	11.58695	0.026383	86.6215	2.40	
0.0000	10900	0.0143	0.0201	0.016278	10.05	0.069586	0.070130	10.53814	0.019796	85.6181	2.29	
0.0000	11900	0.0153	0.0184	0.017416	9.2	0.068227	0.068760	9.61561	0.035415	83.9458	2.13	
0.0000	13000	0.0162	0.0168	0.018440	8.4	0.067004	0.067527	8.79090	0.030962	82.4407	2.00	
0.0000	14000	0.0171	0.0156	0.019465	7.8	0.065781	0.066294	8.09444	0.038008	80.9356	1.88	
0.0000	15000	0.018	0.0146	0.020489	7.3	0.064557	0.065061	7.54586	0.042516	79.4305	1.76	
0.0000	16000	0.0189	0.0137	0.021514	6.85	0.063334	0.063829	7.07142	0.044269	77.9255	1.66	
0.0000	17000	0.0198	0.0129	0.022538	6.45	0.062111	0.062596	6.64699	0.046813	76.4204	1.56	
0.0000	18000	0.0207	0.0121	0.023563	6.05	0.060888	0.061363	6.24680	0.043995	74.9153	1.46	
0.0000	19000	0.0216	0.0115	0.024587	5.75	0.059664	0.060130	5.89809	0.055382	73.4102	1.38	
0.0000	20000	0.0229	0.0109	0.026067	5.45	0.057897	0.058349	5.59799	0.075927	71.2362	1.25	
0.0000	21000	0.0239	0.0104	0.027205	5.2	0.056538	0.056980	5.32353	0.066649	69.5639	1.16	
0.0000	22000	0.0257	0.0099	0.029254	4.95	0.054092	0.054514	5.07346	0.114333	66.5537	1.01	
0.0000	23200	0.0266	0.0094	0.030279	4.7	0.052868	0.053281	4.82338	0.054349	65.0486	0.94	
0.0000	24500	0.0283	0.0089	0.032214	4.45	0.050558	0.050953	4.57329	0.097338	62.2057	0.81	
0.0000	26000	0.0298	0.0084	0.033921	4.2	0.048519	0.048898	4.32319	0.081191	59.6972	0.70	
0.0000	27500	0.0312	0.008	0.035515	4	0.046616	0.046980	4.09878	0.089802	57.3560	0.60	
0.0000	29000	0.0326	0.0075	0.037109	3.75	0.044713	0.045063	3.87298	0.067889	55.0148	0.51	
0.0000	30500	0.0339	0.0072	0.038588	3.6	0.042946	0.043282	3.67423	0.099665	52.8407	0.43	
0.0000	33000	0.0362	0.0066	0.041206	3.3	0.039820	0.040131	3.44674	0.082726	48.9944	0.30	
0.0000	34500	0.0375	0.0063	0.042686	3.15	0.038053	0.038351	3.22413	0.087457	46.8204	0.23	
0.0000	36000	0.0397	0.0061	0.045191	3.05	0.035063	0.035337	3.09960	0.213422	43.1413	0.12	
0.0000	37500	0.0412	0.0058	0.046898	2.9	0.033024	0.033282	2.97405	0.093087	40.6329	0.04	
0.0000	39000	0.0421	0.0056	0.047922	2.8	0.031801	0.032050	2.84956	0.080267	39.1278	0.00	



Sample		KCF Blackstone
Pyknometer type / numbe	Type 3 (Gay-Lussac), nomi	2823
Density of solvent (water)	ρw	0.997
Mass of Pycnometer (g)	m1	32.383
mass of pycnometer + Rock	m2	35.361
Mass of Rock (g)	m2-m1	2.977
Mass of pycnometer + Solv	m4	81.680
Mass of Solvent (g)	m4-m1	49.296
Mass Pycnometer + Rock+ s	m3	82.666
Mass of solvent post-displ	m3-m2	47.306
Mass of displaced solvent (	(m4-m1)-(m3-m2)	1.991
Volume of Pycnometer/solvent (ml)		49.426
Density of solvent (g/ml)	ρw	0.997
Volume of Rock/ displaced solvent (ml)		1.996
Particle Density (g/ml)	((m2-m1)ρw/((m4-m1)-(n	1.491

Appendix IV-d: PCA (Multivariate Analysis) Data

Olefins & Biomarker Parameter Data Matrix for PCA

Data Matrix (Olefins & Biomarker parameters)																																							
	O1	O2	M1a	M1b	M1c	M1d	M1e	M2a	M2b	M2c	M2d	M2e	M3a	M3b	M3c	M3d	M3e	M1f	M1g	M1h	M1i	M1j	M2f	M2g	M3f	M3g	M3h	M3i	M3j	C1a	C2a	C3a	C1b	C2b	C3b	E1a	E2a	E3a	E1b	E2b	E3b
P1	1.2	1.2	1.3	1.2	1.2	1.2	1.2	1.2	1.3	1.2	1.2	1.2	1.3	1.2	1.3	1.3	1.3	1.2	1.2	1.2	1.2	1.3	1.2	1.3	1.2	1.2	1.3	1.2	1.2	1.2	1.3	1.3	1.2	1.2	1.3	0.8	0.8	0.7	0.7	0.8	0.7
P2	0.5	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	2.4	2.3	2.2	2.4	2.4	2.2
P3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	4.8	4.8	4.6	4.9	4.8	4.5
P4	3.9	3.8	4.1	4	4	3.9	3.9	3.8	4.2	4.2	3.7	3.9	4	3.5	3.5	3.8	3.9	3.7	3.7	3.9	3.8	4	3.6	4	4.2	4.1	4.2	4	3.7	4	3	3.5	4	3.2	3.8	1.5	1.6	1.6	1.5	1.7	1.5
P5	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.7	1	1	0.8	0.9
P6	59.6	57.8	56.9	54.4	54.1	53.6	53	49.4	52.6	55.4	53.9	56	55.5	56	56.1	54.3	56.1	53.2	60.6	54.3	55.2	54.7	54	55.5	55.1	54.1	55.3	56.5	57.7	52.4	58.9	56.3	54.1	52.2	54	2.4	3.5	1.9	3	4.7	2.3
P7	1.3	1.4	1	1.1	1	1.2	1.3	1.5	1.3	1.1	1.1	1	1.6	0.9	1	1	1.4	0.9	0.8	1.1	1.2	1.2	1.1	1.2	1.5	1.5	1.3	1.4	1	1	0.9	1.2	1.1	0.7	1.1	0.2	0.2	0.2	0.2	0.2	0.2
P8	1.7	1.5	1.3	1.5	1.4	1.5	1.6	0.8	1.6	1.3	1.5	1.2	1.3	1.5	1.2	1.4	1.6	1.3	1.2	1.6	1.7	1.4	1.5	1.6	1.5	1.7	1.7	1.4	1.6	1.4	1.4	1.1	1.5	1.3	1.4	0.4	0.5	0.5	0.5	0.4	0.6
P9	43.1	42.4	32.7	34.8	34.2	35.9	35.7	30.8	37.3	36.5	37.8	35.6	38.2	35.5	33.9	35.7	39.5	32.8	36.6	36.1	37	37.4	36.7	36.5	39.9	38.5	38.3	38.7	38.6	38.8	41.4	41.7	37.2	35.4	36.6	34	32	31.9	31.8	32	31.1
P10	25.1	25.6	31.6	31.5	35.3	31.3	30	35.9	29.9	32.1	30.7	33	29	33	33.5	33.2	28.2	38.1	35.1	30.2	29.3	29.5	30	28.5	27.5	26.4	27.9	26.1	28.9	30.4	31.8	29.3	29.8	36	31.9	47.6	48.7	49.2	49.5	48.8	49.8
P11	38.8	38.7	40.2	38.6	39	38.5	37.4	37.4	36.4	32.4	37.6	38.5	39.6	37.5	38.8	39.2	38.7	37.2	36.4	39.3	38.5	37.4	40.1	37.1	39.9	38.7	38.1	39.6	42.4	37.1	38.6	38.2	37.5	37.7	39.1	28.2	28	26.9	26.6	27.1	27.1
P12	32.4	32	31.4	31.6	31.2	31.5	29.5	29.7	29.8	33.4	31.6	31.3	31.4	32	31.9	32.1	32	29.9	29.9	31.2	31.3	31.3	31.1	30.1	31.2	31.4	31.6	31.8	29.5	31.9	31.4	30	31.6	31.6	31.8	31.4	31.9	32.6	29.9	28.7	32.1
P13	28.8	29.3	28.4	29.9	29.8	30	33.1	32.8	33.9	34.2	30.9	30.2	29	30.6	29.3	28.7	29.3	33	33.8	29.5	30.2	31.3	28.8	32.8	28.9	29.9	30.3	28.6	28.1	31	30	31.8	30.8	30.7	29.2	40.4	40.1	40.5	43.5	44.2	40.8
P14	0.7	0.7	1	0.9	1	0.9	0.8	1.2	0.8	0.9	0.8	0.9	0.8	0.9	1	0.9	0.7	1.2	1	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.8	0.8	0.7	0.8	1	0.9	1.2	1.3	1.3	1.3	1.3	1.3
P15	12.8	16.7	13.9	14.9	14.6	14.8	14.7	15.2	15.8	13.4	14	13.5	16.1	15.6	14.3	15.2	14.8	66.8	41.2	25	16.2	18.5	21.2	41.7	184.6	63	78.4	75	25.7	14.5	12.9	15.6	33.3	35	47.9	4.8	4.5	6.5	4.8	8.9	6.9
P16	2.9	1.9	2.5	2	2.9	1.9	3	2.2	3	1.9	2	1.9	3	2	3.2	2.1	2.1	1.6	2.9	1.9	3.1	2.9	2.9	3.2	2	2.3	3.6	1.8	2.1	2.6	2.6	3.2	2	1.9	3.4	0.3	0.4	0.4	0.4	0.4	0.4
P17	5.2	5.3	5.1	4.9	4.8	4.8	4.8	4.8	5.9	4.8	5.1	4.9	5.3	5.2	5.1	5.5	4.9	3.9	5.8	4.8	4.9	4.8	4.8	5.3	5.1	4.9	5	4.6	6.1	4.3	4.5	4.7	5.5	4.6	5	0.8	0.7	0.9	1	1	0.9
P18	6.5	6.7	5.6	4.2	5.5	5.5	4	5	6.3	5	5	4.1	5.7	4.7	6.2	5.6	5.7	4.5	5.4	4.2	6.2	4.9	5.1	5.2	4.9	4.8	7.2	4.1	6.4	3.7	4	5.2	5	4.3	3.9	0.2	0.2	0.2	0.2	0.2	0.2
P19	0.8	0.8	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	1	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.7	0.8	0.9	0.2	0.2	0.3	0.2	0.3	0.2
P20	56.5	56.2	56.5	56.1	56.2	56	55.7	56.1	55.8	55.7	55.9	56.1	56.1	56.5	55.9	56.2	55.8	56.3	55.6	56.1	55.7	55.2	55.8	56.3	56.2	55.6	56.2	55.7	56	55.3	54.9	55.9	55.3	54.3	55.3	29.1	29.3	28.1	28.6	26.7	29.5
P21	0.14	0.13	0.14	0.15	0.15	0.15	0.15	0.15	0.11	0.14	0.14	0.15	0.13	0.14	0.14	0.12	0.15	0.19	0.11	0.15	0.15	0.16	0.16	0.14	0.16	0.15	0.15	0.15	0.12	0.14	0.14	0.14	0.11	0.12	0.14	0.95	0.98	0.96	0.95	0.92	0.93
P22	2.1	1.84	2.1	2.1	2.28	2.09	2.28	2.18	2.05	2.13	2.02	2.16	2.01	2.02	2.19	1.96	2.17	2.05	2.11	2.16	2.34	2.3	2.32	2.09	1.99	2.13	2.17	2.13	1.88	2.17	2.18	2.02	1.88	1.92	2.12	0.56	0.56	0.56	0.55	0.54	0.51
P23	1.03	1.04	1.02	1.04	1.09	1.03	1.04	1.02	1.13	0.99	1.14	1	1.04	1.01	1.01	1.1	1.04	1	1.16	0.95	1.01	0.98	0.97	1.12	1.12	1.02	1.01	1.05	1.11	1.02	1.08	1.06	1.1	1.18	1.03	2.12	2.08	2.24	2.44	2.67	2.77
P24	0.65	0.63	0.63	0.65	0.65	0.63	0.62	0.64	0.66	0.63	0.66	0.64	0.63	0.65	0.63	0.66	0.66	0.59	0.65	0.64	0.64	0.64	0.65	0.63	0.64	0.64	0.62	0.66	0.65	0.62	0.63	0.62	0.63	0.63	0.64	0.5	0.56	0.57	0.55	0.57	0.55
P25	0.92	0.97	1.08	0.93	0.94	1.01	1.04	0.92	0.93	1.02	1.02	0.93	0.96	0.91	1.01	0.91	0.91	0.86	0.93	0.91	0.92	0.92	1.08	1.06	1.04	1.05	1.02	0.9	0.93	1.02	0.88	0.96	1.05	0.97	0.93	0.61	0.64	0.67	0.59	0.65	0.67
P26	0.09	0.1	0.1	0.1	0.1	0.1	0.09	0.08	0.11	0.1	0.11	0.12	0.1	0.09	0.1	0.09	0.1	0.11	0.1	0.1	0.1	0.11	0.1	0.1	0.1	0.09	0.1	0.09	0.1	0.09	0.18	0.22	0.13	0.12	0.12	0.38	0.41	0.49	0.51	0.44	0.49
P27	0.18	0.17	0.03	0.06	0.03	0.17	0.09	0.17	0.19	0.18	0.18	0.18	0.05	0.09	0.05	0.06	0.06	0.09	0.11	0.08	0.06	0.18	0.18	0.18	0.05	0.04	0.07	0.06	0.07	0.12	0.2	0.09	0.18	0.21	0.07	1.26	1.73	1.13	1.6	1.57	1.14
P28	4.7	6.33	2.26	2.14	1.55	2.64	1.87	1.22	2.95	3.58	4.56	2.47	1.88	1.16	1.44	1.37	3.61	2.87	1.88	1.13	1.18	5.62	3.55	0.64	0.88	1.13	0.94	0.98	0.99	0.64	0.38	0.93	7.49	0.24	0.16	0	0.01	0.01	0.01	0.02	0.01
H1	2	3	6	7	12	15	26	3	12	17	24	25	8	23	20	18	10	7	10	14	24	16	0	3	6	10	8	5	7	1181	932	690	11	1368	242	49827	44059	54264	0	39130	42004
H2	14	17	16	17	28	30	29	17	30	32	30	39	23	39	40	31	20	18	19	29	31	29	9	22	20	23	23	19	21	365	441	250	47	520	130	2617	0	1779	0	0	0
H3	5	7	10	10	17	19	21	10	18	22	23	26	13	26	24	20	11	10	11	18	21	20	3	12	11	12	13	11	13	339	410	232	16	476	104	12452	10623	12553	0	8985	9600
H4	11	15	13	13	20	20	27	17	21	25	24	34	19	33	32	24	18	15	12	21	25	23	9	16	15	17	17	15	17	153	185	118	28	199	73	578	0	341	0	101	0
H5	5	11	15	16	26	24	31	14	25	23	26	37	20	31	33	26	15	15	16	24	21	24	6	15	14	17	17	15	15	162	213	116	12	211	64	3747	3484	3890	0	2540	2724
H6	9	11	9	13	19	19	22	13	20	20	23	27	17	26	27	24	16	11	12	18	22	23	8	16	13	15	14	15	15	133	161	98	20	172	60	0	0	0	0	0	0
H7	3	8	9	12	18	16	20	9	15	17	18	26	12	23	24	19	14	10	9	17	17	18	4	13	11	11	10	9	11	121	153	88	8	158	50	2945	2750	3241	0	2182	2229
H8	7	8	7	9	12	13	16	10	13	18	15	22	10	19	23	18	13	7	8	14	13	16	6	15	10	11	11	9	13	111	144	84	14	144	48	548	464	556	0	248	0
H9	3	5	8	7	9	11	12	5	10	13	10	18	9	16	16	13	9	7	7	9	8	16	2	10	5	6	6	6	7	102	128	69	6	124	39	1882	2017	2111	0	1473	1361
H10	5	8	7	8	10	13	14	8	13	14	16	18	11	17	16	13	12	7	8	13	12	14	6	12	8	10	10	9	11	111	140	80	13	135	44	0	0	0	0	0	0
H11	2	4	4	6	6	10	13	3	10	8	11	16	6	13	14	10	9	6	6	9	9	11	2	6	4	6	6	5	8	95	130	73	4	113	34	2207	2121	2638	0	1317	1437
HT	65	98	103	118	177	190	230	108	188	209	219	288	148	265	269	216	146	112	119	186	202	209	54	140	117	138	136	118	138	2872	3037	1897	179	3621	886	76802	65518	81372	0	55975	59354
D1	70	99	87	97	146	167	177	79	169	180	191	229	136	249	230	184	124	122	122	175	198	195	65	118	116	149	148	127	146	3572	2962	2331	395	5183	993	54177	53406	57235	392	18174	15840
D2	330	466	409	459	672	791	828	340	800	820	886	1103	631	1119	1066	833	561	580	578	822	882	909	278	534	507	659	653	588	635	12702	10474	8144	1186	17411	3568	203545	214624	211071	2441	110725	106363
D3	35	60	55	78	116	136	150	46	132	144	154	205	103	204	185	129	77	96	91	138	155	141	23	69	77	110	96	83	95	3559	2967	2202	187	4875	815	55314	56030	59314	44135	50765	53221
D4	174	391	381	467	674	830	872	249	785	813	922	1231	608	1158	1026	740	462	566	531	808	923	887	173	415	422	558	546	470	519	14319	11941	9143	650	19346	3729	245721	254545	251507	230196	228732	243688
D5	312	444	394	450	628	752	802	333	754	788	856	1063	612	1068	1013	789	546	542	551	786	844	833	257	521	485	626	623	569	597	11089	9378	7331	1072	15465	3257	149725	162904	188349	993	81398	83855
D6	102	172	155	185	239	294	349	129	292	336	349	461	254	501	440	334	224	215	203	251	361	311	85	200	193	263	213	227	232	8076	6972	5460	742	11556	2262	103654	97299	138088	27214	43308	61723
D7	489	852	797	922	1268	1564	1647	633	1572	1607	1763	2259	1261	2288	2095	1570	1032	1100	1099	1573	1696	1663	404	917	911	1223	1191	1084	1112	31876	27539	21347	2529	44323	8931	482465	473743	557532	192292	261759	280774
D8	36	85	52	99	92	136	131	73	96	158	136	139	141	228	162	131	101	67	85	128	183	132	42	120	115	129	132	155	112	4585	5169	5788	634	7584	2300	120402	135374	153425	70318	118628	135767
D9	238	437	428	503	668	830	890	345	838	865	939	1229	709	1312	1174	830	544	580	575	823	911	837	237	503	533	649	637	567	565	23247	20275	15768	1566	32404	6133	373346	347162	386969	320752	309959	340502
D10	53	77	78	92	117	152	164	121	184	167	179	225	176	358	323	257	146	117	115	161	167	178	49	108	163	180	170	164	154	19261	16399	12051	1643	27001	4757	348149	353689	394131	9389	221689	232633
D11	33	71	79	92	118	157	163	96	182	165	180	234	176	374	327	228	123	107	110	158	142	177	30	97	150	164	157	132	135	21020	18268	13674	947	29118	4990	404874	414573	451020	383604	370399	400824
D12	67	103	90	107	137	176	188	105	182	189	211	257	166	296	283	222	133	117	138	189	190	198	58	120	139	167	159	143	146	7866	6759	5292	750	11330	2195	119535	119358	134572	1357	79205	84112
D13	54.9	119	129	167	212	268	277	189	278	281	309	510	273	516	466	329	199	163	197	294	160	305	58	163	247	256	249	212	220	21059	17859	12478	1948	29177	5293	298905	257070	291675	134057	182504	201168
D14	16.8	36	34	46	63	82	84	48	77	80	104	185	78	152	124	88	57	44	65	89	89	88	16	55	69	80	73	60	70	4439	3319.7	2676	463	6639	1210	78627	53159	64045	9146	29327	31529
D15	50.4	73	85	95	110	139	132	205	188	153	164	132	256	444	364	279	166	100	109	146	132	141	58	100	240	226	194	206	163	24101	21190	17343	3467	35374	7013	498821	430741	481104	67069	374237	426115
D16	20.8	42	51	56	72	92	92	47	101	95	104	110	95	189	159	110	65	67	65	95	94	91	21	46	76	78	79	69	73	7579	6727.5	5282	498	11003	1969	167469	142081	155649	115453	123433	136030
DT	2081.7	3527	3304	3915	5329	6564	6947	3040	6630	6842	7447	9464	5674	10454	9435	7054	4560	4582	4633	6638	7125	7086	1854	4085	4445	5517	5319	4857	4977	218349	188198	146310	18675	307789	59415	4E+06	4E+06	4E+06	2E+06	3E+06	3E+06

IV-d: Acid Data Matrix for PCA

Data Matrix (Acids)																										
	O	M1a	M1b	M1c	M1d	M1e	M1f	M1g	M2a	M2b	M2c	M2d	M2e	M2f	M2g	M3a	M3b	M3c	M3d	M3e	M3f	M3g	Col1	Col2	Col3	Ext1	Ext2	Ext3
A1	0	0	297	0	0	0	0	0	0	295	0	314	0	218	340	0	0	0	0	0	343	0	447	3512	2929	146588	161370	319670
A2	0	0	0	0	0	0	0	0	0	0	0	0	0	285	268	0	0	0	0	0	497	0	2423	6541	5611	156471	147403	323274
A3	0	0	477	0	568	829	748	673	731	754	1305	875	455	1114	1272	783	1126	428	477	603	1584	1014	5867	12245	8356	182280	102302	244856
A4	0	1099	2199	1328	2104	1408	1339	1335	1454	1397	1938	1739	1275	2030	1831	1428	1290	1234	2158	1327	2799	2135	7445	12948	8014	156296	99391	259147
A5	0	3310	8108	599	8873	697	3969	4940	4249	4894	6832	6173	2522	4693	7023	2687	2074	2021	3931	6741	8991	7149	15825	27760	17218	269664	105820	555267
A6	0	307	1103	384	1038	507	799	602	313	0	753	518	0	642	788	0	550	0	0	0	933	615	6870	14700	6743	189255	140871	385971
A7	0	2869	5716	4370	6729	3648	3072	3389	2971	2859	4813	3745	1014	1437	4469	1315	1442	720	1810	1794	4755	3926	11603	22149	10924	211672	103597	327158
A8	0	0	0	0	434	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4090	8618	3737	123410	70848	170787
A9	0	0	265	0	416	0	0	0	0	0	0	0	0	0	301	0	0	0	0	0	0	0	3782	8697	3629	122824	59504	338218
A10	0	0	484	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2648	5437	2295	106418	86867	378018
A11	0	0	292	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4977	11197	4528	150045	41950	188434
A12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2862	5252	2261	89405	21794	228855
A13	0	0	256	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8778	19879	7656	178067	75099	304695
A14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1521	3044	1257	59037	67262	104423
A15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3664	9175	4220	58870	50588	125094
A16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	988	1833	848	45530	31729	240040
A17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2671	5869	2215	59204	75386	237523
A18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1104	2038	907	50838	68579	201110
A19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1991	4403	1715	53193	73816	274123
A20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	901	1051	395	37819	13063	31224
A21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1078	2399	879	37661	69026	235007
A22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	9792	779	0	31345	19342	89137
A23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1217	3257	1729	51639	1157	100011
A24	0	301	838	0	644	378	483	393	319	277	636	601	511	707	760	0	0	0	690	280	1012	573	3099	8646	3421	47897	154610	399642
A25	0	660	1041	997	904	1000	571	830	464	664	1057	708	0	746	1019	0	0	338	430	380	1144	748	3016	6191	3208	59797	75913	186694
ATot	0	2517	13601	1723	12862	0	0	0	82590	4680	5565	9452	5644	0	6154	1968	1954	1375	4973	7866	9095	4145	82590	189531	92976	2646634	1765661	6157466
HA1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	256	304	245	1728	0	0
HA2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	360	1122	791	31996	11834	6542
HA3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1939	7471	3832	228135	61459	47994
HA4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	540	2386	1121	64821	13206	11653
tHA	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3095	11282	5989	326680	86498	66189
AP1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.23	0.26	0.2	0.28	0.73	0.73

IV-d: Olefins and Biomarker Parameter Normalised Data for PCA

Normalised data (Olefins + Biomarker Parameters)																																								
	O1	O2	M1a	M1b	M1c	M1d	M1e	M2a	M2b	M2c	M2d	M2e	M3a	M3b	M3c	M3d	M3e	M1f	M1g	M1h	M1i	M1j	M2f	M2g	M3f	M3g	M3h	M3i	M3j	C1a	C2a	C3a	C1b	C2b	C3b	E1a	E2a	E3a	E1b	E2b	E3b
P1	0.227	0.227	0.719	0.227	0.227	0.227	0.227	0.227	0.719	0.227	0.227	0.227	0.719	0.227	0.719	0.719	0.719	0.227	0.227	0.227	0.227	0.719	0.227	0.719	0.227	0.227	0.719	0.227	0.227	0.227	0.719	0.719	0.227	0.227	0.719	-1.993	-1.993	-2.626	-2.626	-1.993	-2.626
P2	-0.415	-0.415	-0.187	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	-0.415	2.471	2.366	2.257	2.471	2.471	2.257
P3	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	-0.409	2.410	2.410	2.337	2.445	2.410	2.299
P4	0.455	0.366	0.626	0.541	0.541	0.455	0.455	0.366	0.709	0.709	0.276	0.455	0.541	0.090	0.090	0.366	0.455	0.276	0.276	0.455	0.366	0.541	0.184	0.541	0.709	0.626	0.709	0.541	0.276	0.541	-0.415	0.090	0.541	-0.206	0.366	-2.430	-2.262	-2.262	-2.430	-2.100	-2.430
P5	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	0.247	-1.716	-1.716	-1.716	-1.716	0.247	0.247	0.247	0.247	0.247	0.247	0.247	-3.791	2.109	2.109	-1.716	0.247	
P6	0.488	0.457	0.440	0.395	0.389	0.379	0.368	0.296	0.360	0.413	0.385	0.424	0.415	0.424	0.426	0.393	0.426	0.372	0.505	0.393	0.409	0.400	0.387	0.415	0.408	0.389	0.411	0.433	0.455	0.356	0.476	0.430	0.389	0.352	0.387	-2.508	-2.216	-2.673	-2.339	-1.970	-2.539
P7	0.684	0.871	0.068	0.283	0.068	0.488	0.684	1.051	0.684	0.283	0.283	0.068	1.224	-0.158	0.068	0.068	0.871	-0.158	-0.397	0.283	0.488	0.488	0.283	0.488	1.051	1.051	0.684	0.871	0.068	0.068	-0.158	0.488	0.283	-0.648	0.283	-2.183	-2.183	-2.183	-2.183	-2.183	-2.183
P8	0.926	0.528	0.097	0.528	0.317	0.528	0.731	-1.172	0.731	0.097	0.528	-0.133	0.097	0.528	-0.133	0.317	0.731	0.097	-0.133	0.731	0.926	0.317	0.528	0.731	0.528	0.926	0.926	0.317	0.731	0.317	0.317	-0.374	0.528	0.097	0.317	-2.472	-2.115	-2.115	-2.115	-2.472	-1.781
P9	2.056	1.861	-1.211	-0.477	-0.682	-0.109	-0.175	-1.916	0.343	0.087	0.501	-0.208	0.625	-0.241	-0.786	-0.175	1.021	-1.175	0.119	-0.043	0.248	0.375	0.151	0.087	1.141	0.718	0.656	0.779	0.749	0.810	1.578	1.664	0.311	-0.275	0.119	-0.751	-1.466	-1.503	-1.540	-1.466	-1.802
P10	-1.383	-1.281	-0.190	-0.207	0.386	-0.240	-0.460	0.474	-0.477	-0.109	-0.340	0.035	-0.636	0.035	0.114	0.067	-0.781	0.785	0.357	-0.426	-0.583	-0.547	-0.460	-0.726	-0.911	-1.122	-0.836	-1.181	-0.654	-0.391	-0.157	-0.583	-0.495	0.489	-0.141	1.952	2.072	2.125	2.157	2.082	2.189
P11	0.499	0.479	0.780	0.458	0.540	0.438	0.209	0.209	-0.006	-0.923	0.251	0.438	0.661	0.230	0.499	0.580	0.479	0.166	-0.006	0.600	0.438	0.209	0.760	0.145	0.720	0.479	0.355	0.661	1.202	0.145	0.458	0.376	0.230	0.272	0.560	-2.014	-2.069	-2.383	-2.471	-2.325	-2.325
P12	1.176	0.787	0.195	0.394	-0.005	0.295	-1.755	-1.544	-1.439	2.128	0.394	0.096	0.195	0.787	0.690	0.885	0.787	-1.335	-1.335	-0.005	0.096	0.096	-0.105	-1.126	-0.005	0.195	0.394	0.591	-1.755	0.690	0.195	-1.230	0.394	0.394	0.591	0.195	0.690	1.369	-1.335	-2.613	0.885
P13	-0.817	-0.678	-0.929	-0.514	-0.541	-0.487	0.308	0.235	0.502	0.573	-0.248	-0.433	-0.761	-0.327	-0.678	-0.845	-0.678	0.284	0.478	-0.623	-0.433	-0.144	-0.817	0.235	-0.789	-0.514	-0.407	-0.873	-1.015	-0.222	-0.487	-0.016	-0.274	-0.301	-0.705	1.927	1.867	1.947	2.530	2.660	2.008
P14	-1.104	-1.104	0.508	0.000	0.508	0.000	-0.537	1.454	-0.537	0.000	-0.537	0.000	-0.537	0.000	0.508	0.000	-1.104	1.454	0.508	-0.537	-0.537	-0.537	-0.537	-0.537	-1.104	-1.104	-1.104	-1.104	-1.104	-0.537	-0.537	-1.104	-0.537	0.508	0.000	1.454	1.895	1.895	1.895	1.895	1.895
P15	-0.494	-0.163	-0.392	-0.306	-0.331	-0.314	-0.323	-0.281	-0.233	-0.438	-0.384	-0.429	-0.209	-0.249	-0.357	-0.281	-0.314	1.624	0.993	0.348	-0.201	-0.034	0.138	1.008	2.963	1.547	1.834	1.775	0.384	-0.340	-0.485	-0.249	0.717	0.781	1.189	-1.648	-1.718	-1.306	-1.648	-0.936	-1.237
P16	0.733	-0.096	0.430	-0.001	0.733	-0.096	0.804	0.179	0.804	-0.096	-0.001	-0.096	0.804	-0.001	0.941	0.090	0.090	-0.402	0.733	-0.096	0.873	0.733	0.733	0.941	-0.001	0.265	1.195	-0.195	0.090	0.509	0.509	0.941	-0.001	-0.096	1.071	-2.343	-2.136	-2.136	-2.136	-2.136	-2.136
P17	0.487	0.525	0.449	0.369	0.329	0.329	0.329	0.329	0.742	0.329	0.449	0.369	0.525	0.487	0.449	0.600	0.369	-0.073	0.707	0.329	0.369	0.329	0.329	0.525	0.449	0.369	0.409	0.245	0.810	0.114	0.202	0.287	0.600	0.245	0.409	-2.457	-2.593	-2.328	-2.206	-2.206	-2.328
P18	0.748	0.792	0.534	0.134	0.508	0.508	0.068	0.374	0.703	0.374	0.374	0.101	0.559	0.288	0.680	0.534	0.559	0.228	0.482	0.134	0.680	0.346	0.402	0.429	0.346	0.317	0.898	0.101	0.726	-0.036	0.068	0.429	0.374	0.166	0.034	-2.326	-2.326	-2.326	-2.326	-2.326	-2.326
P19	0.358	0.358	0.743	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	1.108	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.358	0.743	0.358	-0.049	0.358	0.743	-2.529	-2.529	-1.959	-2.529	-1.959	-2.529
P20	0.456	0.434	0.456	0.426	0.434	0.419	0.397	0.426	0.404	0.397	0.411	0.426	0.426	0.456	0.411	0.434	0.404	0.441	0.389	0.426	0.397	0.359	0.404	0.441	0.434	0.389	0.434	0.397	0.419	0.366	0.336	0.411	0.366	0.290	0.366	-2.300	-2.272	-2.444	-2.371	-2.654	-2.244
P21	-0.415	-0.461	-0.415	-0.370	-0.370	-0.370	-0.370	-0.370	-0.554	-0.415	-0.415	-0.370	-0.461	-0.415	-0.415	-0.508	-0.370	-0.191	-0.554	-0.370	-0.370	-0.325	-0.325	-0.415	-0.325	-0.370	-0.370	-0.370	-0.508	-0.415	-0.415	-0.415	-0.554	-0.508	-0.415	2.384	2.464	2.411	2.384	2.303	2.331
P22	0.402	0.055	0.402	0.402	0.627	0.390	0.627	0.504	0.338	0.441	0.299	0.479	0.285	0.299	0.516	0.219	0.491	0.338	0.415	0.479	0.699	0.651	0.675	0.390	0.259	0.441	0.491	0.441	0.110	0.491	0.504	0.299	0.110	0.165	0.428	-2.325	-2.325	-2.325	-2.351	-2.376	-2.455
P23	-0.450	-0.424	-0.477	-0.424	-0.291	-0.450	-0.424	-0.477	-0.188	-0.559	-0.162	-0.532	-0.424	-0.505	-0.505	-0.265	-0.424	-0.532	-0.111	-0.670	-0.505	-0.587	-0.614	-0.213	-0.213	-0.477	-0.505	-0.397	-0.239	-0.477	-0.317	-0.370	-0.265	-0.061	-0.450	1.899	1.828	2.105	2.433	2.786	2.933
P24	0.682	0.138	0.138	0.682	0.682	0.138	-0.137	0.411	0.952	0.138	0.952	0.411	0.138	0.682	0.138	0.952	0.952	-0.971	0.682	0.411	0.411	0.411	0.682	0.138	0.411	0.411	-0.137	0.952	0.682	-0.137	0.138	-0.137	0.138	0.138	0.411	-3.570	-1.821	-1.535	-2.108	-1.535	-2.108
P25	0.043	0.402	1.160	0.115	0.187	0.682	0.889	0.043	0.115	0.751	0.751	0.115	0.331	-0.030	0.682	-0.030	-0.030	-0.401	0.115	-0.030	0.043	0.043	1.160	1.025	0.889	0.957	0.751	-0.103	0.115	0.751	-0.251	0.331	0.957	0.402	0.115	-2.416	-2.158	-1.905	-2.590	-2.073	-1.905
P26	-0.547	-0.456	-0.456	-0.456	-0.456	-0.456	-0.547	-0.639	-0.366	-0.456	-0.366	-0.277	-0.456	-0.547	-0.456	-0.547	-0.456	-0.366	-0.456	-0.456	-0.456	-0.366	-0.456	-0.456	-0.456	-0.547	-0.456	-0.547	-0.456	-0.547	0.243	0.576	-0.188	-0.277	-0.277	1.804	2.018	2.568	2.701	2.228	2.568
P27	-0.188	-0.218	-0.672	-0.569	-0.672	-0.218	-0.470	-0.218	-0.158	-0.188	-0.188	-0.188	-0.603	-0.470	-0.603	-0.569	-0.569	-0.470	-0.406	-0.503	-0.569	-0.188	-0.188	-0.188	-0.603	-0.637	-0.536	-0.569	-0.536	-0.374	-0.128	-0.470	-0.188	-0.099	-0.536	2.122	2.794	1.911	2.620	2.579	1.928
P28	1.443	1.869	0.497	0.434	0.081	0.684	0.281	-0.153	0.822	1.073	1.401	0.603	0.287	-0.200	0.007	-0.043	1.084	0.787	0.287	-0.223	-0.184	1.696	1.061	-0.666	-0.435	-0.223	-0.381	-0.347	-0.338	-0.666	-0.958	-0.390	2.117	-1.139	-1.252	-1.503	-1.486	-1.486	-1.486	-1.470	-1.486
H1	-0.884	-0.791	-0.609	-0.565	-0.408	-0.340	-0.170	-0.791	-0.408	-0.302	-0.195	-0.182	-0.527	-0.208	-0.252	-0.284	-0.462	-0.565	-0.462	-0.361	-0.195	-0.320	-1.242	-0.791	-0.609	-0.462	-0.527	-0.659	-0.565	1.059	0.982	0.885	-0.434	1.107	0.545	2.276	2.236	2.304	-1.242	2.198	2.221
H2	-0.424	-0.317	-0.350	-0.317	-0.036	0.003	-0.016	-0.317	0.003	0.040	0.003	0.153	-0.147	0.153	0.168	0.022	-0.226	-0.285	-0.255	-0.016	0.022	-0.016	-0.662	-0.172	-0.226	-0.147	-0.147	-0.255	-0.198	1.455	1.566	1.233	0.260	1.663	0.851	2.613	-2.017	2.386	-2.017	-2.017	-2.017
H3	-0.842	-0.721	-0.586	-0.586	-0.379	-0.334	-0.294	-0.586	-0.356	-0.276	-0.258	-0.208	-0.485	-0.208	-0.240	-0.314	-0.550	-0.586	-0.550	-0.356	-0.294	-0.314	-1.013	-0.516	-0.550	-0.516	-0.485	-0.550	-0.485	0.859	0.939	0.700	-0.403	1.002	0.364	2.377	2.310	2.380	-1.597	2.239	2.267
H4	-0.543	-0.324	-0.426	-0.426	-0.118	-0.118	0.100	-0.235	-0.083	0.044	0.014	0.270	-0.155	0.248	0.225	0.014	-0.194	-0.324	-0.482	-0.083	0.044	-0.017	-0.681	-0.278	-0.324	-0.235	-0.235	-0.324	-0.235	1.394	1.538	1.199	0.127	1.593	0.838	2.399	-2.429	2.000	-2.429	1.082	-2.429
H5	-1.044	-0.674	-0.520	-0.488	-0.241	-0.282	-0.150	-0.555	-0.261	-0.304	-0.241	-0.059	-0.375	-0.150	-0.118	-0.241	-0.520	-0.520	-0.488	-0.282	-0.350	-0.282	-0.961	-0.520	-0.555	-0.457	-0.457	-0.520	-0.520	0.718	0.863	0.541	-0.631	0.858	0.228	2.391	2.352	2.411	-1.999	2.184	2.221
H6	-0.280	-0.142	-0.280	-0.025	0.246	0.246	0.352	-0.025	0.283	0.283	0.384	0.501	0.166	0.473	0.501	0.415	0.122	-0.142	-0.081	0.207	0.352	0.384	-0.360	0.122	-0.025	0.076	0.027	0.076	0.076	1.689	1.833	1.459	0.283	1.883	1.092	-2.028	-2.028	-2.028	-2.028	-2.028	-2.028
H7	-1.076	-0.650	-0.595	-0.457	-0.258	-0.317	-0.206	-0.595	-0.348	-0.287	-0.258	-0.074	-0.457	-0.136	-0.114	-0.231	-0.382	-0.545	-0.595	-0.287	-0.287	-0.258	-0.959	-0.418	-0.499	-0.499	-0.545	-0.595	-0.499	0.718	0.840	0.552	-0.650	0.857	0.260	2.389	2.353	2.439	-1.803	2.231	2.243
H8	-0.678	-0.594	-0.678	-0.519	-0.332	-0.279	-0.140	-0.451	-0.279	-0.061	-0.184	0.075	-0.451	-0.024	0.106	-0.061	-0.279	-0.678	-0.594	-0.230	-0.279	-0.140	-0.774	-0.184	-0.451	-0.389	-0.389	-0.519	-0.279	1.205	1.389	1.008	-0.230	1.389	0.615	2.339	2.221	2.349	-2.162	1.775	-2.162
H9	-0.892	-0.678	-0.464	-0.526	-0.408	-0.312	-0.270	-0.678	-0.358	-0.231	-0.358	-0.069	-0.408	-0.128	-0.128	-0.231	-0.408	-0.526	-0.526	-0.408	-0.464	-0.128	-1.044	-0.358	-0.678	-0.596	-0.596	-0.596	-0.526	0.823	0.942	0.619	-0.596	0.925	0.324	2.356	2.393	2.417	-1.623	2.227	2.185
H10	-0.457	-0.129	-0.225	-0.129	0.033	0.228	0.284	-0.129	0.228	0.284	0.385	0.475	0.103	0.431	0.385	0.228	0.168	-0.225	-0.129	0.228	0.168	0.284	-0.333	0.168	-0.129	0.033	0.033	-0.044	0.103	1.909	2.095	1.647	0.228	2.066	1.172	-1.906	-1.906	-1.906	-1.906	-1.906	-1.906
H11	-0.943	-0.684	-0.684	-0.514	-0.514	-0.285	-0.163	-0.797	-0.285	-0.387	-0.241	-0.065	-0.514	-0.163	-0.128	-0.285	-0.333	-0.514	-0.514	-0.333	-0.333	-0.241	-0.943	-0.514	-0.684	-0.514	-0.514	-0.592	-0.387	0.812	0.970	0.680	-0.684	0.899	0.301	2.400	2.380	2.491	-1.500	2.139	2.183
HT	-0.769	-0.594	-0.573	-0.515	-0.342	-0.311	-0.229	-0.553	-0.316	-0.270	-0.250	-0.133	-0.418	-0.169	-0.162	-0.256	-0.424	-0.537	-0.512	-0.320	-0.285	-0.270	-0.848	-0.442	-0.519	-0.448	-0.454	-0.515	-0.448	0.857	0.881	0.678	-0.337	0.957	0.350	2.273	2.204	2.298	-2.575	2.137	2.162
D1	-0.896	-0.722	-0.787	-0.732	-0.526	-0.459	-0.429	-0.835	-0.453	-0.421	-0.391	-0.299	-0.562	-0.257	-0.297	-0.410	-0.609	-0.617	-0.617	-0.435	-0.372	-0.380	-0.933	-0.634	-0.642	-0.516	-0.519	-0.597	-0.526	1.095	1.000	0.878	-0.023	1.284	0.445	2.476	2.469	2.504	-0.027	1.921	1.851
D2	-0.880	-0.703	-0.770	-0.711	-0.515	-0.431	-0.408	-0.865	-0.425	-0.413	-0.373	-0.260	-0.547	-0.253	-0.278	-0.405	-0.608	-0.591	-0.592	-0.411	-0.375	-0.360	-0.968	-0.633	-0.660	-0.525	-0.530	-0.584	-0.544	0.997	0.898	0.769	-0.223	1.160	0.344	2.425	2.453	2.444	0.148	2.112	2.091
D3	-0.987	-0.764	-0.800	-0.656	-0.490	-0.424	-0.383	-0.874	-0.436	-0.400	-0.372	-0.252	-0.540	-0.254	-0.295	-0.446	-0.661	-0.569	-0.591	-0.418	-0.369	-0.409	-1.157	-0.706	-0.661	-0.512	-0.569	-0.630	-0.573	0.948	0.872	0.746	-0.290	1.081	0.328	2.104	2.109	2.133	2.009	2.068	2.088
D4	-1.072	-0.716	-0.728	-0.638	-0.477	-0.385	-0.364	-0.915	-0.410	-0.394	-0.339	-0.212	-0.522	-0.239	-0.292	-0.436	-0.643	-0.554	-0.582	-0.397	-0.338	-0.356	-1.074	-0.690	-0.683	-0.560	-0.570	-0.635	-0.592	0.870	0.789	0.672	-0.493	1.002	0.277	2.122	2.138	2.133	2.094	2.091	2.119
D5	-0.886	-0.699	-0.762	-0.692	-0.515	-0.419	-0.385	-0.851	-0.417	-0.394	-0.350	-0.235	-0.528	-0.232	-0.260	-0.393	-0.589	-0.593	-0.584	-0.395	-0.357	-0.364	-0.989	-0.614	-0.652	-0.516	-0.519	-0.567	-0.541	1.013	0.923	0.792	-0.230	1.190	0.361	2.398	2.443	2.520	-0.271	2.073	2.089
D6	-0.968	-0.729	-0.777	-0.696	-0.578	-0.483	-0.404	-0.861	-0.486	-0.422	-0.404	-0.276	-0.550	-0.238	-0.298	-0.425	-0.608	-0.627	-0.653	-0.556	-0.389	-0.457	-1.051	-0.660	-0.676	-0.534	-0.631	-0.602	-0.592	1.042	0.974	0.861	-0.058	1.207	0.455	2.217	2.188	2.349	1.601	1.815	1.978
D7	-0.980	-0.722	-0.753	-0.686	-0.538	-0.440	-0.416	-0.860	-0.438	-0.428	-0.385	-0.269	-0.540	-0.264	-0.304	-0.439	-0.633	-0.604	-0.604	-0.438	-0.403	-0.412	-1.069	-0.688	-0.691	-0.555	-0.567	-0.611	-0.599	0.961	0.893	0.775	-0.217	1.114	0.369	2.224	2.216	2.291	1.796	1.940	1.972
D8	-0.992	-0.671	-0.855	-0.614	-0.642	-0.495	-0.509	-0.728	-0.626	-0.438	-0.495	-0.486	-0.481	-0.300	-0.429	-0.509	-0.607	-0.761	-0.671	-0.518	-0.383	-0.506	-0.935	-0.542	-0.558	-0.515	-0.506	-0.445	-0.568	0.838	0.883	0.926	0.087	1.029	0.576	2.078	2.123	2.170	1.874	2.073	2.124
D9	-0.985	-0.729	-0.738	-0.670	-0.550	-0.459	-0.429	-0.829	-0.455	-0.441	-0.407	-0.293	-0.525	-0.266	-0.313	-0.459	-0.637	-0.610	-0.614	-0.462	-0.420	-0.455	-0.987	-0.670	-0.646	-0.563	-0.570	-0.620	-0.621	0.948	0.890	0.784	-0.191	1.088	0.385	2.120	2.089	2.135	2.056	2.041	2.081
D10	-0.940	-0.809	-0.805	-0.746	-0.662	-0.569	-0.542	-0.650	-0.501	-0.536	-0.511	-0.430	-0.517	-0.265	-0.302	-0.383	-0.583	-0.662	-0.668	-0.549	-0.536	-0.513	-0.968	-0.690	-0.544	-0.509	-0.529	-0.542	-0.564	1.155	1.097	0.987	0.277	1.275	0.656	2.186	2.192	2.230	0.898	2.025	2.043
D11	-1.029	-0.785	-0.751	-0.702	-0.622	-0.530	-0.518	-0.689	-0.482	-0.514	-0.486	-0.401	-0.493	-0.249	-0.292	-0.409	-0.609	-0.654	-0.645	-0.528	-0.562	-0.491	-1.060	-0.685	-0.545	-0.516	-0.530	-0.586	-0.579	1.061	1.015	0.921	0.053	1.167	0.593	2.023	2.030	2.058	2.005	1.994	2.019
D12	-0.911	-0.730	-0.787	-0.714	-0.609	-0.504	-0.476	-0.722	-0.489	-0.473	-0.427	-0.343	-0.528	-0.283	-0.302	-0.405	-0.622	-0.676	-0.606	-0.473	-0.471	-0.454	-0.971	-0.665	-0.603	-0.526	-0.547	-0.591	-0.583	1.112	1.047	0.943	0.112	1.267	0.569	2.271	2.270	2.321	0.364	2.095	2.121
D13	-1.100	-0.815	-0.785	-0.689	-0.600	-0.513	-0.501	-0.643	-0.500	-0.496	-0.460	-0.274	-0.506	-0.269	-0.307	-0.437	-0.624	-0.698	-0.628	-0.479	-0.705	-0.465	-1.080	-0.698	-0.544	-0.530	-0.541	-0.600	-0.587	1.114	1.053	0.919	0.226	1.236	0.599	2.104	2.048	2.095	1.805	1.920	1.956
D14	-1.120	-0.823	-0.846	-0.726	-0.601	-0.496	-0.486	-0.709	-0.521	-0.506	-0.400	-0.169	-0.516	-0.248	-0.330	-0.467	-0.641	-0.744	-0.589	-0.463	-0.463	-0.467	-1.138	-0.655	-0.565	-0.506	-0.542	-0.621	-0.559	1.118	1.000	0.912	0.202	1.281	0.591	2.283	2.124	2.199	1.411	1.883	1.912
D15	-0.951	-0.830	-0.780	-0.743	-0.695	-0.617	-0.634	-0.489	-0.517	-0.586	-0.563	-0.634	-0.415	-0.232	-0.298	-0.386	-0.559	-0.726	-0.698	-0.601	-0.634	-0.613	-0.905	-0.726	-0.436	-0.456	-0.507	-0.487	-0.565	1.099	1.056	0.989	0.453	1.227	0.687	2.109	2.060	2.097	1.440	2.013	2.056
D16	-1.011	-0.775	-0.709	-0.677	-0.591	-0.506	-0.506	-0.737	-0.474	-0.495	-0.464	-0.445	-0.495	-0.258	-0.318	-0.445	-0.626	-0.615	-0.626	-0.495	-0.499	-0.510	-1.008	-0.744	-0.572	-0.563	-0.559	-0.605	-0.586	1.025	0.983	0.899	0.078	1.154	0.556	2.102	2.044	2.076	1.972	1.995	2.029
DT	-0.958	-0.738	-0.765	-0.694	-0.566	-0.479	-0.455	-0.800	-0.475	-0.462	-0.426	-0.326	-0.540	-0.285	-0.328	-0.449	-0.631	-0.629	-0.624	-0.474	-0.445	-0.447	-1.006	-0.677	-0.641	-0.551	-0.567	-0.605	-0.594	0.983	0.921	0.816	-0.043	1.126	0.440	2.164	2.148	2.194	1.816	2.017	2.052

IV-d: Acid Normalised Data for PCA

Normalised Data (Acids)																										
	O	M1a	M1b	M1c	M1d	M1e	M1f	M1g	M2a	M2b	M2c	M2d	M2e	M2f	M2g	M3a	M3b	M3c	M3d	M3e	M3f	M3g	Col1	Col2	Col3	Ext1	Ext2	Ext3
A1	-0.772	-0.772	0.552	-0.772	-0.772	-0.772	-0.772	-0.772	-0.772	0.551	-0.772	0.565	-0.772	0.480	0.583	-0.772	-0.772	-0.772	-0.772	-0.772	0.585	-0.772	0.647	1.126	1.083	1.993	2.015	2.174
A2	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	-0.635	0.635	0.621	-0.635	-0.635	-0.635	-0.635	-0.635	0.759	-0.635	1.114	1.337	1.303	2.050	2.036	2.213
A3	-2.275	-2.275	-0.202	-2.275	-0.144	-0.017	-0.052	-0.087	-0.059	-0.049	0.135	0.001	-0.218	0.082	0.127	-0.036	0.086	-0.239	-0.202	-0.124	0.200	0.051	0.640	0.887	0.759	1.794	1.600	1.894
A4	-3.639	-0.371	-0.048	-0.283	-0.068	-0.256	-0.279	-0.280	-0.241	-0.259	-0.107	-0.157	-0.302	-0.085	-0.133	-0.249	-0.296	-0.317	-0.056	-0.283	0.065	-0.061	0.521	0.779	0.556	1.942	1.730	2.178
A5	-3.801	-0.217	0.179	-0.972	0.219	-0.905	-0.136	-0.040	-0.106	-0.044	0.104	0.059	-0.337	-0.062	0.116	-0.309	-0.423	-0.435	-0.141	0.098	0.225	0.124	0.475	0.724	0.512	1.729	1.315	2.048
A6	-1.483	0.000	0.331	0.058	0.315	0.130	0.247	0.174	0.005	-1.483	0.232	0.135	-1.483	0.191	0.244	-1.483	0.151	-1.483	-1.483	-1.483	0.288	0.180	0.804	1.001	0.799	1.662	1.586	1.847
A7	-3.768	-0.137	0.177	0.054	0.251	-0.028	-0.106	-0.062	-0.122	-0.139	0.098	-0.016	-0.611	-0.453	0.065	-0.493	-0.451	-0.767	-0.347	-0.351	0.093	0.005	0.499	0.794	0.472	1.823	1.498	2.022
A8	-0.550	-0.550	-0.550	-0.550	0.855	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	-0.550	1.373	1.546	1.352	2.161	2.033	2.236
A9	-0.638	-0.638	0.636	-0.638	0.738	-0.638	-0.638	-0.638	-0.638	-0.638	-0.638	-0.638	-0.638	-0.638	0.665	-0.638	-0.638	-0.638	-0.638	-0.638	-0.638	-0.638	1.241	1.431	1.232	2.035	1.870	2.266
A10	-0.546	-0.546	0.882	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	-0.546	1.275	1.441	1.242	2.128	2.081	2.421
A11	-0.549	-0.549	0.762	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	1.416	1.603	1.394	2.202	1.907	2.254
A12	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	1.429	1.576	1.372	2.264	1.922	2.492
A13	-0.549	-0.549	0.680	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	-0.549	1.462	1.643	1.431	2.128	1.937	2.247
A14	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	1.327	1.500	1.280	2.239	2.272	2.382
A15	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	-0.507	1.459	1.679	1.493	2.124	2.088	2.304
A16	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	-0.495	1.256	1.412	1.217	2.228	2.136	2.650
A17	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	-0.502	1.383	1.571	1.338	2.123	2.180	2.454
A18	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	1.253	1.406	1.204	2.208	2.283	2.551
A19	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	1.332	1.524	1.296	2.125	2.204	2.520
A20	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	-0.498	1.395	1.438	1.166	2.435	2.139	2.381
A21	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	-0.496	1.248	1.448	1.197	2.135	2.286	2.592
A22	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	-0.450	1.990	1.318	-0.450	2.299	2.171	2.577
A23	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	-0.499	1.408	1.672	1.502	2.414	1.394	2.591
A24	-1.767	-0.075	0.227	-1.767	0.150	-0.008	0.064	0.003	-0.058	-0.100	0.146	0.129	0.081	0.177	0.199	-1.767	-1.767	-1.767	0.170	-0.097	0.283	0.115	0.615	0.919	0.644	1.426	1.773	2.055
A25	-2.063	0.050	0.198	0.184	0.152	0.185	0.003	0.124	-0.065	0.052	0.203	0.073	-2.063	0.090	0.191	-2.063	-2.063	-0.167	-0.089	-0.129	0.229	0.091	0.544	0.778	0.564	1.516	1.593	1.886
ATot	-1.828	-0.056	0.326	-0.142	0.313	-1.828	-1.828	-1.828	0.734	0.084	0.123	0.243	0.127	-1.828	0.146	-0.112	-0.113	-0.193	0.098	0.202	0.235	0.057	0.734	0.922	0.761	1.518	1.427	1.709
HA1	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	-0.397	2.147	2.226	2.127	3.021	-0.397	-0.397
HA2	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	-0.500	1.214	1.544	1.443	2.519	2.230	2.057
HA3	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	-0.503	1.309	1.632	1.472	2.450	2.136	2.077
HA4	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	-0.501	1.230	1.638	1.430	2.546	2.109	2.074
tHA	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	-0.505	1.350	1.649	1.502	2.425	2.119	2.057
AP1	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	-0.451	0.880	1.035	0.721	1.136	3.072	3.072

IV-d: Olefins and Biomarker Parameter Transformed Data for PCA

Transformed Data (Log(X+1))- Olefins and Biomarker Parameters																																							
	O1	O2	M1a	M1b	M1c	M1d	M1e	M2a	M2b	M2c	M2d	M2e	M3a	M3b	M3c	M3d	M3e	M1f	M1g	M1h	M1i	M1j	M2f	M2g	M3f	M3g	M3h	M3i	M3j	C1a	C2a	C3a	C1b	C2b	C3b	E1a	E2a	E3a	E1b	E2b	E3b
P1	0.788	0.788	0.833	0.788	0.788	0.788	0.788	0.788	0.833	0.788	0.788	0.788	0.833	0.788	0.833	0.833	0.833	0.788	0.788	0.788	0.788	0.833	0.788	0.833	0.788	0.788	0.833	0.788	0.788	0.788	0.833	0.833	0.788	0.788	0.833	0.588	0.588	0.531	0.531	0.588	0.531
P2	0.405	0.405	0.470	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	1.224	1.194	1.163	1.224	1.224	1.163
P3	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	0.405	1.758	1.758	1.723	1.775	1.758	1.705
P4	1.589	1.569	1.629	1.609	1.609	1.589	1.589	1.569	1.649	1.649	1.548	1.589	1.609	1.504	1.504	1.569	1.589	1.548	1.548	1.589	1.569	1.609	1.526	1.609	1.649	1.629	1.649	1.609	1.548	1.609	1.386	1.504	1.609	1.435	1.569	0.916	0.956	0.956	0.916	0.993	0.916
P5	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.588	0.588	0.588	0.588	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.642	0.531	0.693	0.693	0.588	0.642
P6	4.104	4.074	4.059	4.015	4.009	4.000	3.989	3.920	3.982	4.032	4.006	4.043	4.034	4.043	4.045	4.013	4.045	3.993	4.121	4.013	4.029	4.020	4.007	4.034	4.027	4.009	4.031	4.052	4.072	3.978	4.093	4.048	4.009	3.974	4.007	1.224	1.504	1.065	1.386	1.740	1.194
P7	0.833	0.875	0.693	0.742	0.693	0.788	0.833	0.916	0.833	0.742	0.742	0.693	0.956	0.642	0.693	0.693	0.875	0.642	0.588	0.742	0.788	0.788	0.742	0.788	0.916	0.916	0.833	0.875	0.693	0.693	0.642	0.788	0.742	0.531	0.742	0.182	0.182	0.182	0.182	0.182	0.182
P8	0.993	0.916	0.833	0.916	0.875	0.916	0.956	0.588	0.956	0.833	0.916	0.788	0.833	0.916	0.788	0.875	0.956	0.833	0.788	0.956	0.993	0.875	0.916	0.956	0.916	0.993	0.993	0.875	0.956	0.875	0.875	0.742	0.916	0.833	0.875	0.336	0.405	0.405	0.405	0.336	0.470
P9	3.786	3.770	3.517	3.578	3.561	3.608	3.603	3.459	3.645	3.624	3.658	3.600	3.669	3.597	3.552	3.603	3.701	3.520	3.627	3.614	3.638	3.648	3.630	3.624	3.711	3.676	3.671	3.681	3.679	3.684	3.747	3.754	3.643	3.595	3.627	3.555	3.497	3.493	3.490	3.497	3.469
P10	3.262	3.281	3.484	3.481	3.592	3.475	3.434	3.608	3.431	3.500	3.456	3.526	3.401	3.526	3.541	3.532	3.374	3.666	3.586	3.440	3.411	3.418	3.434	3.384	3.350	3.311	3.364	3.300	3.398	3.447	3.490	3.411	3.428	3.611	3.493	3.884	3.906	3.916	3.922	3.908	3.928
P11	3.684	3.681	3.718	3.679	3.689	3.676	3.648	3.648	3.622	3.509	3.653	3.676	3.704	3.651	3.684	3.694	3.681	3.643	3.622	3.696	3.676	3.648	3.716	3.640	3.711	3.681	3.666	3.704	3.770	3.640	3.679	3.669	3.651	3.656	3.691	3.374	3.367	3.329	3.318	3.336	3.336
P12	3.509	3.497	3.478	3.484	3.472	3.481	3.418	3.424	3.428	3.538	3.484	3.475	3.478	3.497	3.493	3.500	3.497	3.431	3.431	3.472	3.475	3.475	3.469	3.437	3.472	3.478	3.484	3.490	3.418	3.493	3.478	3.434	3.484	3.484	3.490	3.478	3.493	3.515	3.431	3.391	3.500
P13	3.395	3.411	3.381	3.431	3.428	3.434	3.529	3.520	3.552	3.561	3.463	3.440	3.401	3.453	3.411	3.391	3.411	3.526	3.550	3.418	3.440	3.475	3.395	3.520	3.398	3.431	3.444	3.388	3.371	3.466	3.434	3.490	3.459	3.456	3.408	3.723	3.716	3.726	3.795	3.811	3.733
P14	0.531	0.531	0.693	0.642	0.693	0.642	0.588	0.788	0.588	0.642	0.588	0.642	0.588	0.642	0.693	0.642	0.531	0.788	0.693	0.588	0.588	0.588	0.588	0.588	0.531	0.531	0.531	0.531	0.531	0.588	0.588	0.531	0.588	0.693	0.642	0.788	0.833	0.833	0.833	0.833	0.833
P15	2.625	2.874	2.701	2.766	2.747	2.760	2.754	2.785	2.821	2.667	2.708	2.674	2.839	2.809	2.728	2.785	2.760	4.217	3.742	3.258	2.845	2.970	3.100	3.754	5.224	4.159	4.374	4.331	3.285	2.741	2.632	2.809	3.535	3.584	3.890	1.758	1.705	2.015	1.758	2.293	2.067
P16	1.361	1.065	1.253	1.099	1.361	1.065	1.386	1.163	1.386	1.065	1.099	1.065	1.386	1.099	1.435	1.131	1.131	0.956	1.361	1.065	1.411	1.361	1.361	1.435	1.099	1.194	1.526	1.030	1.131	1.281	1.281	1.435	1.099	1.065	1.482	0.262	0.336	0.336	0.336	0.336	0.336
P17	1.825	1.841	1.808	1.775	1.758	1.758	1.758	1.758	1.932	1.758	1.808	1.775	1.841	1.825	1.808	1.872	1.775	1.589	1.917	1.758	1.775	1.758	1.758	1.841	1.808	1.775	1.792	1.723	1.960	1.668	1.705	1.740	1.872	1.723	1.792	0.588	0.531	0.642	0.693	0.693	0.642
P18	2.015	2.041	1.887	1.649	1.872	1.872	1.609	1.792	1.988	1.792	1.792	1.629	1.902	1.740	1.974	1.887	1.902	1.705	1.856	1.649	1.974	1.775	1.808	1.825	1.775	1.758	2.104	1.629	2.001	1.548	1.609	1.825	1.792	1.668	1.589	0.182	0.182	0.182	0.182	0.182	0.182
P19	0.588	0.588	0.642	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.693	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.588	0.642	0.588	0.531	0.588	0.642	0.182	0.182	0.262	0.182	0.262	0.182
P20	4.052	4.047	4.052	4.045	4.047	4.043	4.038	4.045	4.040	4.038	4.041	4.045	4.045	4.052	4.041	4.047	4.040	4.048	4.036	4.045	4.038	4.029	4.040	4.048	4.047	4.036	4.047	4.038	4.043	4.031	4.024	4.041	4.031	4.013	4.031	3.405	3.411	3.371	3.388	3.321	3.418
P21	0.131	0.122	0.131	0.140	0.140	0.140	0.140	0.140	0.104	0.131	0.131	0.140	0.122	0.131	0.131	0.113	0.140	0.174	0.104	0.140	0.140	0.148	0.148	0.131	0.148	0.140	0.140	0.140	0.113	0.131	0.131	0.131	0.104	0.113	0.131	0.668	0.683	0.673	0.668	0.652	0.658
P22	1.131	1.044	1.131	1.131	1.188	1.128	1.188	1.157	1.115	1.141	1.105	1.151	1.102	1.105	1.160	1.085	1.154	1.115	1.135	1.151	1.206	1.194	1.200	1.128	1.095	1.141	1.154	1.141	1.058	1.154	1.157	1.105	1.058	1.072	1.138	0.445	0.445	0.445	0.438	0.432	0.412
P23	0.708	0.713	0.703	0.713	0.737	0.708	0.713	0.703	0.756	0.688	0.761	0.693	0.713	0.698	0.698	0.742	0.713	0.693	0.770	0.668	0.698	0.683	0.678	0.751	0.751	0.703	0.698	0.718	0.747	0.703	0.732	0.723	0.742	0.779	0.708	1.138	1.125	1.176	1.235	1.300	1.327
P24	0.501	0.489	0.489	0.501	0.501	0.489	0.482	0.495	0.507	0.489	0.507	0.495	0.489	0.501	0.489	0.507	0.507	0.464	0.501	0.495	0.495	0.495	0.501	0.489	0.495	0.495	0.482	0.507	0.501	0.482	0.489	0.482	0.489	0.489	0.495	0.405	0.445	0.451	0.438	0.451	0.438
P25	0.652	0.678	0.732	0.658	0.663	0.698	0.713	0.652	0.658	0.703	0.703	0.658	0.673	0.647	0.698	0.647	0.647	0.621	0.658	0.647	0.652	0.652	0.732	0.723	0.713	0.718	0.703	0.642	0.658	0.703	0.631	0.673	0.718	0.678	0.658	0.476	0.495	0.513	0.464	0.501	0.513
P26	0.086	0.095	0.095	0.095	0.095	0.095	0.086	0.077	0.104	0.095	0.104	0.113	0.095	0.086	0.095	0.086	0.095	0.104	0.095	0.095	0.095	0.104	0.095	0.095	0.095	0.086	0.095	0.086	0.095	0.086	0.166	0.199	0.122	0.113	0.113	0.322	0.344	0.399	0.412	0.365	0.399
P27	0.166	0.157	0.030	0.058	0.030	0.157	0.086	0.157	0.174	0.166	0.166	0.166	0.049	0.086	0.049	0.058	0.058	0.086	0.104	0.077	0.058	0.166	0.166	0.166	0.049	0.039	0.068	0.058	0.068	0.113	0.182	0.086	0.166	0.191	0.068	0.815	1.004	0.756	0.956	0.944	0.761
P28	1.740	1.992	1.182	1.144	0.936	1.292	1.054	0.798	1.374	1.522	1.716	1.244	1.058	0.770	0.892	0.863	1.528	1.353	1.058	0.756	0.779	1.890	1.515	0.495	0.631	0.756	0.663	0.683	0.688	0.495	0.322	0.658	2.139	0.215	0.148	0.000	0.010	0.010	0.010	0.020	0.010
H1	1.099	1.386	1.946	2.079	2.565	2.773	3.296	1.386	2.565	2.890	3.219	3.258	2.197	3.178	3.045	2.944	2.398	2.079	2.398	2.708	3.219	2.833	0.000	1.386	1.946	2.398	2.197	1.792	2.079	7.075	6.838	6.538	2.485	7.222	5.493	10.816	10.693	10.902	0.000	10.575	10.646
H2	2.708	2.890	2.833	2.890	3.367	3.434	3.401	2.890	3.434	3.497	3.434	3.689	3.178	3.689	3.714	3.466	3.045	2.944	2.996	3.401	3.466	3.401	2.303	3.135	3.045	3.178	3.178	2.996	3.091	5.903	6.091	5.525	3.871	6.256	4.875	7.870	0.000	7.484	0.000	0.000	0.000
H3	1.792	2.079	2.398	2.398	2.890	2.996	3.091	2.398	2.944	3.135	3.178	3.296	2.639	3.296	3.219	3.045	2.485	2.398	2.485	2.944	3.091	3.045	1.386	2.565	2.485	2.565	2.639	2.485	2.639	5.829	6.019	5.451	2.833	6.168	4.654	9.430	9.271	9.438	0.000	9.103	9.170
H4	2.485	2.773	2.639	2.639	3.045	3.045	3.332	2.890	3.091	3.258	3.219	3.555	2.996	3.526	3.497	3.219	2.944	2.773	2.565	3.091	3.258	3.178	2.303	2.833	2.773	2.890	2.890	2.773	2.890	5.037	5.226	4.779	3.367	5.298	4.304	6.361	0.000	5.835	0.000	4.625	0.000
H5	1.792	2.485	2.773	2.833	3.296	3.219	3.466	2.708	3.258	3.178	3.296	3.638	3.045	3.466	3.526	3.296	2.773	2.773	2.833	3.219	3.091	3.219	1.946	2.773	2.708	2.890	2.890	2.773	2.773	5.094	5.366	4.762	2.565	5.357	4.174	8.229	8.156	8.266	0.000	7.840	7.910
H6	2.303	2.485	2.303	2.639	2.996	2.996	3.135	2.639	3.045	3.045	3.178	3.332	2.890	3.296	3.332	3.219	2.833	2.485	2.565	2.944	3.135	3.178	2.197	2.833	2.639	2.773	2.708	2.773	2.773	4.898	5.088	4.595	3.045	5.153	4.111	0.000	0.000	0.000	0.000	0.000	0.000
H7	1.386	2.197	2.303	2.565	2.944	2.833	3.045	2.303	2.773	2.890	2.944	3.296	2.565	3.178	3.219	2.996	2.708	2.398	2.303	2.890	2.890	2.944	1.609	2.639	2.485	2.485	2.398	2.303	2.485	4.804	5.037	4.489	2.197	5.069	3.932	7.988	7.920	8.084	0.000	7.688	7.710
H8	2.079	2.197	2.079	2.303	2.565	2.639	2.833	2.398	2.639	2.944	2.773	3.135	2.398	2.996	3.178	2.944	2.639	2.079	2.197	2.708	2.639	2.833	1.946	2.773	2.398	2.485	2.485	2.303	2.639	4.718	4.977	4.443	2.708	4.977	3.892	6.308	6.142	6.323	0.000	5.517	0.000
H9	1.386	1.792	2.197	2.079	2.303	2.485	2.565	1.792	2.398	2.639	2.398	2.944	2.303	2.833	2.833	2.639	2.303	2.079	2.079	2.303	2.197	2.833	1.099	2.398	1.792	1.946	1.946	1.946	2.079	4.635	4.860	4.248	1.946	4.828	3.689	7.541	7.610	7.655	0.000	7.296	7.217
H10	1.792	2.197	2.079	2.197	2.398	2.639	2.708	2.197	2.639	2.708	2.833	2.944	2.485	2.890	2.833	2.639	2.565	2.079	2.197	2.639	2.565	2.708	1.946	2.565	2.197	2.398	2.398	2.303	2.485	4.718	4.949	4.394	2.639	4.913	3.807	0.000	0.000	0.000	0.000	0.000	0.000
H11	1.099	1.609	1.609	1.946	1.946	2.398	2.639	1.386	2.398	2.197	2.485	2.833	1.946	2.639	2.708	2.398	2.303	1.946	1.946	2.303	2.303	2.485	1.099	1.946	1.609	1.946	1.946	1.792	2.197	4.564	4.875	4.304	1.609	4.736	3.555	7.700	7.660	7.878	0.000	7.184	7.271
HT	4.190	4.595	4.644	4.779	5.182	5.252	5.442	4.691	5.242	5.347	5.394	5.666	5.004	5.583	5.598	5.380	4.990	4.727	4.787	5.231	5.313	5.347	4.007	4.949	4.771	4.934	4.920	4.779	4.934	7.963	8.019	7.549	5.193	8.195	6.788	11.249	11.090	11.307	0.000	10.933	10.991
D1	4.263	4.605	4.477	4.585	4.990	5.124	5.182	4.382	5.136	5.198	5.257	5.438	4.920	5.521	5.442	5.220	4.828	4.812	4.812	5.170	5.293	5.278	4.190	4.779	4.762	5.011	5.004	4.852	4.990	8.181	7.994	7.754	5.981	8.553	6.902	10.900	10.886	10.955	5.974	9.808	9.670
D2	5.802	6.146	6.016	6.131	6.512	6.675	6.720	5.832	6.686	6.711	6.788	7.007	6.449	7.021	6.973	6.726	6.332	6.365	6.361	6.713	6.783	6.813	5.631	6.282	6.230	6.492	6.483	6.378	6.455	9.450	9.257	9.005	7.079	9.765	8.180	12.224	12.277	12.260	7.801	11.615	11.575
D3	3.584	4.111	4.025	4.369	4.762	4.920	5.017	3.850	4.890	4.977	5.043	5.328	4.644	5.323	5.226	4.868	4.357	4.575	4.522	4.934	5.050	4.956	3.178	4.248	4.357	4.710	4.575	4.431	4.564	8.178	7.996	7.698	5.236	8.492	6.704	10.921	10.934	10.991	10.695	10.835	10.882
D4	5.165	5.971	5.945	6.148	6.515	6.723	6.772	5.521	6.667	6.702	6.828	7.116	6.412	7.055	6.934	6.608	6.138	6.340	6.277	6.696	6.829	6.789	5.159	6.031	6.047	6.326	6.304	6.155	6.254	9.569	9.388	9.121	6.479	9.870	8.224	12.412	12.447	12.435	12.347	12.340	12.404
D5	5.746	6.098	5.979	6.111	6.444	6.624	6.688	5.811	6.627	6.671	6.753	6.970	6.418	6.974	6.922	6.672	6.304	6.297	6.314	6.668	6.739	6.726	5.553	6.258	6.186	6.441	6.436	6.346	6.394	9.314	9.146	8.900	6.978	9.646	8.089	11.917	12.001	12.146	6.902	11.307	11.337
D6	4.635	5.153	5.050	5.226	5.481	5.687	5.858	4.868	5.680	5.820	5.858	6.136	5.541	6.219	6.089	5.814	5.416	5.375	5.318	5.529	5.892	5.743	4.454	5.303	5.268	5.576	5.366	5.429	5.451	8.997	8.850	8.605	6.611	9.355	7.724	11.549	11.486	11.836	10.212	10.676	11.030
D7	6.194	6.749	6.682	6.828	7.146	7.356	7.407	6.452	7.361	7.383	7.475	7.723	7.140	7.736	7.648	7.359	6.940	7.004	7.003	7.361	7.437	7.417	6.004	6.822	6.816	7.110	7.083	6.989	7.015	10.370	10.223	9.969	7.836	10.699	9.097	13.087	13.068	13.231	12.167	12.475	12.545
D8	3.611	4.454	3.970	4.605	4.533	4.920	4.883	4.304	4.575	5.069	4.920	4.942	4.956	5.434	5.094	4.883	4.625	4.220	4.454	4.860	5.215	4.890	3.761	4.796	4.754	4.868	4.890	5.050	4.727	8.431	8.551	8.664	6.454	8.934	7.741	11.699	11.816	11.941	11.161	11.684	11.819
D9	5.476	6.082	6.061	6.223	6.506	6.723	6.792	5.846	6.732	6.764	6.846	7.115	6.565	7.180	7.069	6.723	6.301	6.365	6.356	6.714	6.816	6.731	5.472	6.223	6.280	6.477	6.458	6.342	6.339	10.054	9.917	9.666	7.357	10.386	8.722	12.830	12.758	12.866	12.678	12.644	12.738
D10	3.989	4.357	4.369	4.533	4.771	5.030	5.106	4.804	5.220	5.124	5.193	5.421	5.176	5.883	5.781	5.553	4.990	4.771	4.754	5.088	5.124	5.187	3.912	4.691	5.100	5.198	5.142	5.106	5.043	9.866	9.705	9.397	7.405	10.204	8.468	12.760	12.776	12.884	9.147	12.309	12.357
D11	3.526	4.277	4.382	4.533	4.779	5.063	5.100	4.575	5.209	5.112	5.198	5.460	5.176	5.927	5.793	5.434	4.820	4.682	4.710	5.069	4.963	5.182	3.434	4.585	5.017	5.106	5.063	4.890	4.913	9.953	9.813	9.523	6.854	10.279	8.515	12.911	12.935	13.019	12.857	12.822	12.901
D12	4.220	4.644	4.511	4.682	4.927	5.176	5.242	4.663	5.209	5.247	5.357	5.553	5.118	5.694	5.649	5.407	4.898	4.771	4.934	5.247	5.252	5.293	4.078	4.796	4.942	5.124	5.075	4.970	4.990	8.970	8.819	8.574	6.621	9.335	7.694	11.691	11.690	11.810	7.214	11.280	11.340
D13	4.024	4.787	4.868	5.124	5.361	5.595	5.628	5.247	5.631	5.642	5.737	6.236	5.613	6.248	6.146	5.799	5.298	5.100	5.288	5.687	5.081	5.724	4.078	5.100	5.513	5.549	5.521	5.361	5.398	9.955	9.790	9.432	7.575	10.281	8.574	12.608	12.457	12.583	11.806	12.115	12.212
D14	2.879	3.611	3.555	3.850	4.159	4.419	4.443	3.892	4.357	4.394	4.654	5.226	4.369	5.030	4.828	4.489	4.060	3.807	4.190	4.500	4.500	4.489	2.833	4.025	4.248	4.394	4.304	4.111	4.263	8.398	8.108	7.892	6.140	8.801	7.099	11.272	10.881	11.067	9.121	10.286	10.359
D15	3.940	4.304	4.454	4.564	4.710	4.942	4.890	5.328	5.242	5.037	5.106	4.890	5.549	6.098	5.900	5.635	5.118	4.615	4.700	4.990	4.890	4.956	4.078	4.615	5.485	5.425	5.273	5.333	5.100	10.090	9.961	9.761	8.151	10.474	8.856	13.120	12.973	13.084	11.113	12.833	12.962
D16	3.082	3.761	3.951	4.043	4.290	4.533	4.533	3.871	4.625	4.564	4.654	4.710	4.564	5.247	5.075	4.710	4.190	4.220	4.190	4.564	4.554	4.522	3.091	3.850	4.344	4.369	4.382	4.248	4.304	8.933	8.814	8.572	6.213	9.306	7.586	12.029	11.864	11.955	11.657	11.723	11.821
DT	7.641	8.168	8.103	8.273	8.581	8.790	8.846	8.020	8.800	8.831	8.916	9.155	8.644	9.255	9.152	8.861	8.425	8.430	8.441	8.801	8.872	8.866	7.526	8.315	8.400	8.616	8.579	8.488	8.513	12.294	12.145	11.893	9.835	12.637	10.992	15.125	15.087	15.196	14.291	14.773	14.857

IV-d: Acids Transformed Data for PCA

Transformed Data (Log(X+1))- Acids																										
	O	M1a	M1b	M1c	M1d	M1e	M1f	M1g	M2a	M2b	M2c	M2d	M2e	M2f	M2g	M3a	M3b	M3c	M3d	M3e	M3f	M3g	Col1	Col2	Col3	Ext1	Ext2	Ext3
A1	0.000	0.000	5.697	0.000	0.000	0.000	0.000	0.000	0.000	5.690	0.000	5.753	0.000	5.389	5.832	0.000	0.000	0.000	0.000	0.000	5.841	0.000	6.105	8.164	7.983	11.895	11.991	12.675
A2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.656	5.595	0.000	0.000	0.000	0.000	0.000	6.211	0.000	7.793	8.786	8.633	11.961	11.901	12.686
A3	0.000	0.000	6.170	0.000	6.344	6.721	6.619	6.513	6.596	6.627	7.175	6.775	6.122	7.017	7.149	6.664	7.027	6.061	6.170	6.404	7.368	6.923	8.677	9.413	9.031	12.113	11.536	12.408
A4	0.000	7.003	7.696	7.192	7.652	7.251	7.200	7.197	7.283	7.243	7.570	7.462	7.151	7.616	7.513	7.265	7.163	7.119	7.677	7.191	7.937	7.667	8.915	9.469	8.989	11.960	11.507	12.465
A5	0.000	8.105	9.001	6.397	9.091	6.548	8.287	8.505	8.355	8.496	8.830	8.728	7.833	8.454	8.857	7.897	7.638	7.612	8.277	8.816	9.104	8.875	9.669	10.231	9.754	12.505	11.570	13.227
A6	0.000	5.730	7.007	5.953	6.946	6.230	6.685	6.402	5.749	0.000	6.625	6.252	0.000	6.466	6.671	0.000	6.312	0.000	0.000	0.000	6.839	6.423	8.835	9.596	8.816	12.151	11.856	12.864
A7	0.000	7.962	8.651	8.383	8.814	8.202	8.030	8.129	7.997	7.959	8.479	8.228	6.923	7.271	8.405	7.182	7.274	6.581	7.502	7.493	8.467	8.276	9.359	10.006	9.299	12.263	11.548	12.698
A8	0.000	0.000	0.000	0.000	6.075	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	8.317	9.062	8.226	11.723	11.168	12.048
A9	0.000	0.000	5.583	0.000	6.033	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.710	0.000	0.000	0.000	0.000	0.000	0.000	0.000	8.238	9.071	8.197	11.719	10.994	12.731
A10	0.000	0.000	6.184	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.882	8.601	7.739	11.575	11.372	12.843
A11	0.000	0.000	5.680	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	8.513	9.323	8.418	11.919	10.644	12.147
A12	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.960	8.567	7.724	11.401	9.989	12.341
A13	0.000	0.000	5.549	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	9.080	9.897	8.943	12.090	11.227	12.627
A14	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.328	8.021	7.137	10.986	11.116	11.556
A15	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	8.207	9.124	8.348	10.983	10.831	11.737
A16	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.897	7.514	6.744	10.726	10.365	12.389
A17	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.891	8.678	7.703	10.989	11.230	12.378
A18	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.008	7.620	6.811	10.836	11.136	12.212
A19	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.597	8.390	7.448	10.882	11.209	12.521
A20	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.805	6.958	5.981	10.541	9.478	10.349
A21	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.984	7.783	6.780	10.536	11.142	12.367
A22	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	9.189	6.659	0.000	10.353	9.870	11.398
A23	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.105	8.089	7.456	10.852	7.054	11.513
A24	0.000	5.710	6.732	0.000	6.469	5.938	6.182	5.976	5.768	5.628	6.457	6.400	6.238	6.562	6.635	0.000	0.000	0.000	6.538	5.638	6.921	6.353	8.039	9.065	8.138	10.777	11.949	12.898
A25	0.000	6.494	6.949	6.906	6.808	6.909	6.349	6.723	6.142	6.500	6.964	6.564	0.000	6.616	6.928	0.000	0.000	5.826	6.066	5.943	7.043	6.619	8.012	8.731	8.074	10.999	11.237	12.137
ATot	0.000	7.831	9.518	7.452	9.462	0.000	0.000	0.000	11.322	8.451	8.624	9.154	8.639	0.000	8.725	7.585	7.578	7.227	8.512	8.970	9.116	8.330	11.322	12.152	11.440	14.789	14.384	15.633
HA1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.549	5.720	5.505	7.455	0.000	0.000
HA2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	5.889	7.024	6.675	10.373	9.379	8.786
HA3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.570	8.919	8.251	12.338	11.026	10.779
HA4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.293	7.778	7.023	11.079	9.489	9.363
tHA	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	8.038	9.331	8.698	12.697	11.368	11.100
AP1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.207	0.231	0.182	0.247	0.548	0.548